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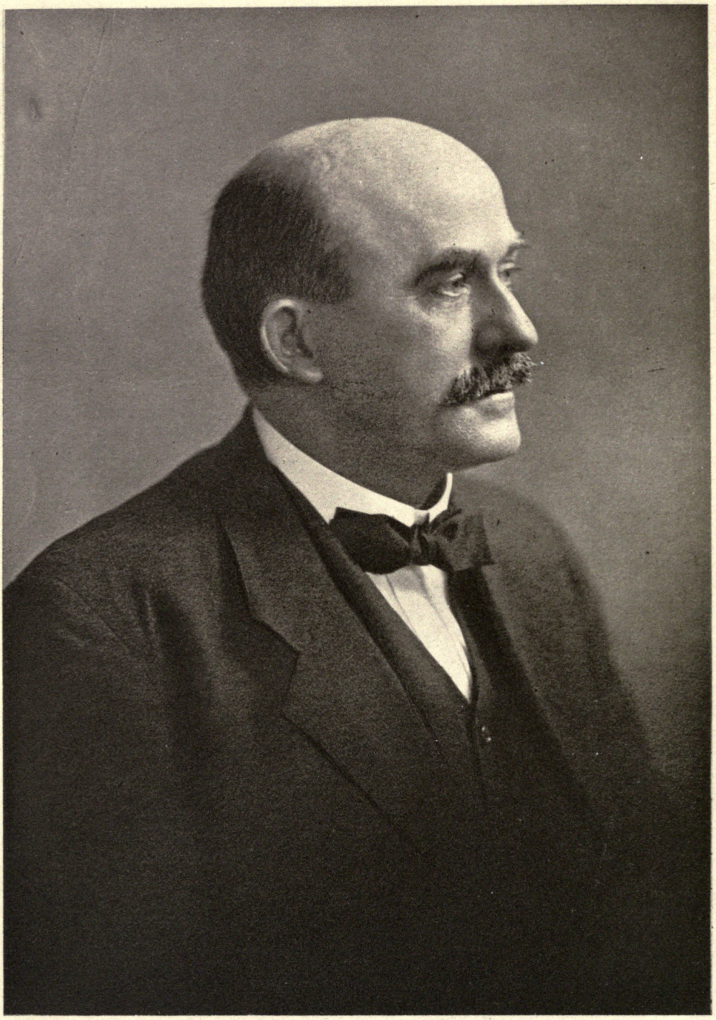

Very Sincerely
H. C. Jones

THE NATURE OF SOLUTION

BY
HARRY C. JONES
LATE PROFESSOR OF PHYSICAL CHEMISTRY IN THE
JOHNS HOPKINS UNIVERSITY

WITH A BIOGRAPHICAL SKETCH BY
E. EMMET REID
PROFESSOR OF ORGANIC CHEMISTRY IN THE
JOHNS HOPKINS UNIVERSITY

AND TRIBUTES BY
PROFESSORS ARRHENIUS,
OSTWALD AND WOODWARD

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PREFACE

No subject in chemistry has received more attention, especially during the last quarter of a century, than that of solution. This is due primarily to the fundamental significance of solution for chemical science.

Solutions in the broad sense of the term are fundamental not only for chemistry, but for geology and the various branches of biology. Matter in the pure, homogeneous condition is relatively inert. It becomes active when mixed in a certain way with other matter in the same or in a different state of aggregation — when dissolved.

Since solution is so fundamental for the natural sciences in general, and for chemistry in particular, we must know what solutions are, if we would ever make these various branches of science exact. Since chemistry has to do largely with the science of solution, it can become an exact science only by the science of solution becoming exact. We must first know what is the real condition of matter in solution. What laws does it obey? Is the dissolved substance combined with the solvent, and if so with how much of it?

As we shall see, many of these questions have now been answered and the relations between solutions and gases accurately established. This is of the greatest importance. We really know something about matter in the gaseous state, and we can now apply this knowledge to matter in the dissolved condition; and this has done more than any other one discovery to place the science of solution upon an exact basis.

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The very intensive work done in this laboratory on the nature of solution has been carried out largely with the aid of grants from the Carnegie Institution of Washington, without which much of the work could not have been completed and many of the results obtained could not have been published.

The Carnegie Institution has generously allowed me to make free use of Chapter VII, No. 210, Publication of the Carnegie Institution of Washington, especially in preparing chapters XI, XIV, and XV of this work. The Franklin Institute of Philadelphia has also allowed me to use parts of one of my recent papers in their Journal.

In preparing Chapter II many references to the literature have been obtained with the aid of the admirable little book by Walden, "Die Lösungstheorien in ihrer geschichtlichen Aufeinanderfolge."

In addition to true solutions we have colloidal solutions, which have come very prominently to the front in the last ten or fifteen years. While most of our knowledge in this field is still empirical, yet much of value has been learned, and the importance of colloids for the science of living, as well as of dead matter, is beginning to be realized. In preparing the chapter on colloids, I would express my indebtedness to the comprehensive work of Freundlich, "Kapillarchemie," especially for references to the literature on colloidal chemistry. This is the great hand-book in this field.

Many references to the literature on solutions have been obtained with the aid of my "Elements of Physical Chemistry," 4th Ed. (The Macmillan Co., N.Y.), to which the student desiring a systematic discussion of physical chemistry is referred.

The present work is not a text-book, but a general discussion of some of the more important properties of solutions, true and colloidal. It is therefore written in a nonmathematical, indeed, largely in a semi-popular style.

It is hoped that this work may interest students of the various branches of science to go on into the real physical chemistry of solutions, and from this into physical chemistry in its broadest sense.

HARRY C. JONES.

BIOGRAPHICAL SKETCH

> **"The man or woman, who does work worth doing, is the man or woman who lives, breathes and sleeps that work; with whom it is ever present in his, or her soul; whose ambition it is to do it well and feel rewarded by the thought of having done it well. That man, that woman, puts the whole country under an obligation." — RUSKIN.**

FEW men of science have ever worked with such consuming intensity as did the late Professor Harry Clary Jones. His tremendous energy was at once an inspiration and a despair to those associated with him. His enthusiasm was contagious, yet few could hold the pace he set.

In the fifty years of his life he lived more than most who reach three score and ten, and into his twenty years of scientific activity he crowded enough work to last several men a lifetime. Work was his vocation, his vacation, his duty, his dissipation, his life, his death.

He was a large man possessing great physical force and a strength which never seemed to tire. He worked long hours at his laboratory and went home to read proof. In summer he would go away for a vacation, but would spend it writing a book; when a bright Saturday afternoon came, he would get away to the country, but to spend the hours riding over his three farms telling his farmers how to raise more corn and wheat on his fertile fields.

There is something strange about this farmer boy leaving the well-tilled acres of his father and his father's father and coming to the city, to the University, where by unremitting labor he forged his way to the front. In sight of his birth-place, a stately brick house built by his grandfather, still stands a tiny country school-house where his early education was obtained, and, hard by, a little Methodist church of which he was a member in his youth, and to which he always contributed. His remains repose in this church-yard in sight of the school-house and the farm. Well nigh the entire population of the surrounding country came together to do him last honors. They had heard of his scientific achievements but to them he was a fellow farmer, a leading citizen, and a benefactor of the community.

To the end of his life he managed that farm efficiently and profitably, and to it added two adjoining farms which he managed equally well, so that he really was one of the large farmers in one of the most fertile portions of Maryland, but farming was never allowed to interfere with his scientific work.

Professor Jones was born near New London, a village in Frederick County, Maryland (U. S. A.), November 11th, 1865, and there spent his early years. The reading of one of Tyndall's books on science awakened his interest in physical science and gave him the impulse to seek a college education. At the age of twenty he entered Johns Hopkins University as a "special student," his preparation not being sufficient for regular matriculation, but his deficiencies were soon made up and he passed to the degree of bachelor of arts in 1889. His untiring industry and mental alertness were already conspicuous in his undergraduate years.

He remained at the University for graduate work taking chemistry as major with physics and mathematics as minor subjects.

Two scholarships as an undergraduate, and two more scholarships and a fellowship in his three years as a graduate student testify to his merits. His first research was carried out under Professor H. N. Morse, "On the Action of Metallic Cadmium on the Halogen Salts of Cadmium" and on "A Redetermination of the Atomic Weight of Cadmium."

He received the degree of Doctor of Philosophy from the Johns Hopkins University in June, 1892. He felt drawn to physical chemistry, which was at that time becoming differentiated from the older chemistry and which had come into prominence on account of the work of van't Hoff, Ostwald, and Arrhenius. Hence Dr. Jones crossed the ocean to study with these three leaders, and worked with Ostwald at Leipzig, Arrhenius at Stockholm, and van't Hoff at Amsterdam. The two years spent in this way made him a thorough-going physical chemist, and into physical chemistry he flung himself with consuming ardor. The reader will find from the contents of this book how highly Dr. Jones valued these three men and how their ideas permeated his thinking. He renewed his acquaintance with them in his frequent summer trips to Europe. Professor Ostwald and Professor Arrhenius were his close friends till his death.

In the fall of 1894 he returned to the Johns Hopkins University as a Fellow by Courtesy. This was a purely honorary position giving him the use of the laboratory but requiring nothing of him. He gave a few lectures in physical chemistry but spent the most of his time on research. The next year he was appointed Instructor in Physical Chemistry, being promoted in 1898 to Associate. In 1900 he was made Associate Professor and in 1903, Professor of Physical Chemistry in Johns Hopkins University, which position he retained to the time of his death. In 1902 he married Miss Harriet Brooks, a member of one of the old families of Baltimore, who survives him.

He carried out a piece of research in the laboratory of Arrhenius on the hydrates of sulphuric acid, mention of which is made on pages 46–48 of the present volume. Thus began his work on hydrates in solution. After his return to this country he began a systematic study of the deviations, found in more concentrated solutions, from the laws of gas pressure and the theory of electrolytic dissociation. From 1903 on he was enabled to enlarge this work by generous grants from the Carnegie Institution of Washington. These grants were continued till the time of his death and the same Institution has, since his death, provided for the rounding out and completion of several of his investigations.

His earlier work was on the abnormalities in the molecular depression of the freezing point in aqueous solutions of certain substances which separate from solution with water of crystallization. In 1900 he offered the following as a tentative explanation: "In concentrated solutions these substances must take up a part of the water forming complex compounds with it and thus removing it from the field of action as far as freezing-point lowering is concerned. . . . The lowering of the freezing point is thus abnormally great, because a part of the water is no longer present as solvent. . . . We do not put forward the above suggestion as the final statement of a theory, but only as a tentative explanation which, however, seems to account for the experimental facts which have been brought to light." This was his first statement of the hydrate theory which was the central thought in all of his subsequent work. His work spread out in ever-widening circles, but the idea of hydrates, or solvates, to use the more general term, always remained the center.

In 1901 he undertook the study of the conductivity and dissociation of electrolytes and their temperature coefficients. This study was carried over into non-aqueous and mixed solvents, and parallel investigations were carried out on the viscosity of the solutions, showing the important bearing of viscosity on conductance and arriving at an explanation of various phenomena connected with viscosity, *e.g.* negative viscosity coefficients. Using the conductivity method, many inorganic substances and organic acids were studied in water solution. By a vast number of measurements it was shown that these temperature coefficients are greater in the case of the more hydrated substances indicating a breaking down of the hydrates with elevation of temperature.

A large amount of work, extending over several years, was done on the absorption spectra of solutions. This involved observations on thousands of solutions in several solvents and in many mixed solvents. Four of the ten monographs published by the Carnegie Institution of Washington, embodying his investigations, are devoted to this spectrographic work. More recently this was extended farther down the spectrum, as well as made more quantitative in character, by the use of a radiomicrometer with a fine grating spectroscope. With this apparatus the ionization constants of indicators and the light absorption coefficients of solutions were studied in addition to the phenomena of solvation. The spectrographic evidence showed that in general, the light absorption is characteristic of the combination of the solute, *i.e.* the solvate with the solvent rather than of the solute alone.

All in all, he investigated sixteen lines of evidence bearing on the presence of solvates in solution. In this he was aided by a large number of advanced students and assistants. Counting up the time his various coworkers put on this study would make one hundred and fifteen years for one worker. A summary of all these investigations is given in Chapter VII, Publication 210, of the Carnegie Institution of Washington. The last two chapters of the present volume are mainly an exposition of his own work on solvation. His own conclusion is: "The theory of electrolytic dissociation, supplemented by the theory of solvation, is then not simply a theory of dilute or ideal solutions, but a theory of solutions in general."

Before his work began, the idea of solvation had been frequently suggested and, contemporaneously with his work, various important investigations have been carried out along somewhat similar lines by other investigators, yet the amount and variety of evidence which he obtained on the existence and behavior of solvates give him a preëminent place in connection with the theory of solvation. His work has gone far toward obtaining general recognition of the great importance of solvation in many phenomena, not only in the field of chemistry, but also of biology and other sciences.

He was a man of marked personality with strong likes and dislikes. He was a pioneer and a promoter of physical chemistry in America, a champion of a cause, an advocate rather than a judge. He was not easily shaken from an opinion but, on sufficient evidence, would quickly and frankly acknowledge an error.

He was an enthusiastic teacher and a remarkably clear lecturer; he spoke rapidly but the right word seldom failed him. Those who worked under him enjoyed considerable liberty of thought and action. In every way he showed a keen interest in them and was quick to aid them, looking out for their advancement even years after they had left the University.

His laboratory was a place of intense chemical activity. In twenty years fifty-seven persons carried on research under his guidance, about fifty of whom did their doctorial dissertation work with him. Many of these remained one or two years as Carnegie assistants, after receiving the doctor's degree. Professor Jones and his collaborators published one hundred and forty articles in American, German, English, and French journals. Ten monographs written by Professor Jones, embodying his investigations, have been published by the Carnegie Institution of Washington and one is now being prepared.

Professor Jones was a writer of books, the present volume being the twelfth, for the student of chemistry and the general reader of science. He wrote with great facility and amazing rapidity, in one case writing a book in six weeks, yet his style was good, always readable and clear.

He maintained that by writing slowly one loses force and charm. Many readers have found his more popular books as difficult as a novel to lay aside. Several of his books have been quite successful, his "Elements of Physical Chemistry" having gone through four editions and having been translated into Italian and Russian, while others have been reprinted several times. All in all about 20,000 copies of Professor Jones' books have been sold.

A bibliography of his articles and books is to be found in the appendix to this volume. The most of this is taken from the Johns Hopkins University Circular of February, 1916.

In his youth he studied the piano and debated long between it and science but never touched it after he made his decision for science. He retained his fondness for music and was a frequent and appreciative hearer of the best. He was a genial host and loved to entertain his friends in his well-appointed home. His students, in particular, look back with pleasure to informal dinners with him and Mrs. Jones. He traveled extensively in Europe and in America.

He was a member of the American Chemical Society, the American Physical Society, the Franklin Institute, American Philosophical Society, and Washington Academy of Science, and honorary member of the Brooklyn Institute of Arts and Sciences.

He was an associate editor of the *Zeitschrift für physikalishe Chemie,* the *Journal de Chemie physique* and *Journal of the Franklin Institute.* In 1913 he was the Longstreth Medalist of the Franklin Institute. His unremitting work and an inherited tendency to nervousness brought on insomnia and melancholia which made his last months almost unbearable and led to his untimely death on April 9, 1916. He learned many things but never learned to rest.

The present volume was written by Professor Jones during the last summer of his life and put into the hands of the printer, but later he withdrew it from publication. After his death it was decided to issue it as a memorial volume. The writer of this sketch has supervised bringing it out. Professor E. C. Bingham, of Lafayette College, has kindly read the proof and made valuable suggestions. The burden of correcting the proof, verifying references, making indexes, etc., has been borne by Dr. Jones' Carnegie assistants, Dr. P. B. Davis and Dr. H. H. Lloyd, and thanks are due them for their faithful work.

His work is all on record and his place in Chemistry will best be decided by the chemists of the future, but a few tributes from some who are well able to judge are not out of place at this time.

E. EMMET REID.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, MD.
January, 1917.

CONTENTS

CHAPTER I

IMPORTANCE OF SOLUTION

PAGE

Importance of Solution Early Recognized 1
Types of Solutions.. 1
State of Aggregation a Function of Conditions.................... 3
Aqueous Solutions the More Important 4
Present Use of the Term Solution............................. 5
Solution and Chemical Transformation.......................... 6
Solution Fundamental for all Branches of Chemistry................ 7
Dry Substances do not Generally React Chemically.................. 7
Dry Chlorine and Dry Sodium................................ 8
Dry Hydrochloric Acid Gas on Dry Carbonates 8
Dry Acids on Dry Litmus.................................... 9
Dry Ammonium Chloride Sublimes Undecomposed.................. 9
Dry Hydrochloric Acid Gas on Dry Ammonia Gas 9
Dry Sulphuric Acid on Dry Metallic Sodium...................... 11
Importance of Solution for Physics............................ 12
Solution and Geology...................................... 13
Solution and Biology....................................... 14
Water a Remarkable Compound............................... 16
Heat Evolved in the Formation of Water........................ 17
Physical Properties of Water 17
Importance of Solution Justifies the Work Expended upon It 19

CHAPTER II

EARLIER VIEWS AS TO THE NATURE OF SOLUTION

Sir Isaac Newton.. 20
Boerhaave 21
Wallerius.. 22
Lavoisier.. 22
Fourcroy 23
Klaproth.. 23
Berthollet... 23
Thomson.. 25
Grotthuss... 25
Berzelius' Electrochemical Theory............................ 27
Berzelius' Theory of Solution 29
Gay-Lussac.. 30

Williamson........ 31
Clausius........ 33
Kopp........ 35
Guldberg and Waage........ 35
Valson........ 36
Favre and Valson........ 38
Landolt........ 39
Gladstone........ 39
Kohlrausch........ 40
Berthelot........ 40
Thomsen........ 42
Raoult........ 43
Mendeléeff........ 44
Testing Mendeléeff's Hypothesis........ 46
End of the Qualitative Period........ 48

CHAPTER III

The Osmotic Pressure of Solutions

Traube's Method of Measuring Osmotic Pressure........ 50
Pfeffer's Preparation of Semi-permeable Membranes........ 50
Pfeffer's Measurements........ 51
Pfeffer's Results........ 52
Where Pfeffer Left the Subject of Osmotic Pressure........ 53
Other Measurements of Osmotic Pressure........ 55
Work of Berkeley and Hartley on the Osmotic Pressures of Concentrated Solutions........ 55
Results Obtained........ 56
Pfeffer's Membranes would not Withstand Great Pressures........ 58
Electrical Method of Preparing Semi-permeable Membranes........ 58
Measurements of Osmotic Pressure made by Morse, Frazer, Holland and Co-workers........ 59
Results with Cane Sugar........ 60
Ratios between Gas Pressure and Osmotic Pressure........ 60
Summary of Relations........ 62
Results with Glucose........ 63
Results with Mannite........ 64
Osmotic Pressure of an Electrolyte........ 64
Results with Lithium Chloride........ 65
Durability of the Morse Cells........ 66
Cell for High Osmotic Pressures........ 66
De Vries' Method of Measuring the Relative Osmotic Pressures of Solutions........ 67
Method of Procedure........ 69
Isotonic Coefficients........ 69
Limitations of the Method........ 70
Other Methods of Determining the Relative Osmotic Pressures of Solutions........ 70

CHAPTER IV

RELATIONS BETWEEN SOLUTIONS AND GASES DEMONSTRATED BY VAN'T HOFF

Law of Boyle Applies to the Osmotic Pressures of Dilute Solutions..... 73
Law of Gay-Lussac Applies to the Osmotic Pressure of Dilute Solutions. 74
Work of Soret.. 75
Equality of Gas Pressure and of Osmotic Pressure................... 76
Importance of the Applicability of the Gas Laws to Solutions......... 78
Exceptions to the Above Relations.................................. 79

CHAPTER V

THE THEORY OF ELECTROLYTIC DISSOCIATION AS ANNOUNCED BY ARRHENIUS

Arrhenius and the Dissociation Theory............................... 82
Arrhenius Points out Methods of Measuring the Magnitude of Dissociation.. 83
Dissociation from Freezing-point Lowering Compared with Dissociation from Conductivity... 84
Bearing of the Theory of Electrolytic Dissociation on Chemistry...... 86
Opposition to the Theory of Electrolytic Dissociation................ 87
Relations between Solutions and Gases and the Theory of Electrolytic Dissociation hold only for Dilute Solutions........................ 88

CHAPTER VI

DIFFUSION IN SOLUTION

The Phenomenon of Diffusion... 90
Diffusion Caused by Some Force..................................... 90
Work of Graham on Diffusion... 91
The Generalization of Fick... 93
Effect of Mass on Diffusion.. 93
Temperature Coefficients of Diffusion — Principle of Soret........... 96
Osmotic Pressure Produces Diffusion................................. 96
Importance of Osmotic Pressure for Chemistry........................ 99
Bearing of Osmotic Pressure on Biological Phenomena............... 99
Osmotic Pressure and Geology....................................... 101

CHAPTER VII

DEPRESSION OF THE VAPOR-TENSION OF A SOLVENT BY SUBSTANCES DISSOLVED IN IT

Work of Faraday... 103
Investigations of Wüllner.. 104
Study of Vapor-tension by Walker.................................... 104

Raoult and the Vapor-tensions of Solvents and of Solutions........... 106
Raoult's Results — Effect of Concentration 107
Effect of Temperature... 108
Effect of Nature of Dissolved Substance............................ 109
Raoult's Law — Effect of Nature of Solvent......................... 110
Frazer-Lovelace Method of Measuring Vapor-tension 111
The Boiling-point Method... 114
Boiling-point Method of Beckmann................................... 115
Boiling-point Apparatus of Jones................................... 116
Molecular Weights from Boiling-point Determinations................ 117
Electrolytic Dissociation Measured by the Boiling-point Method 118
Molecular Weights of the Metals in Mercury......................... 119

CHAPTER VIII

DEPRESSION OF THE FREEZING-POINT OF A SOLVENT BY THE SOLUTE

Investigations of Raoult 122
Results obtained by Raoult 123
Raoult's Law of Freezing-point Lowering............................ 126
The Freezing-point Method of Beckmann.............................. 127
Results of Molecular Weight Determinations by the Freezing-point Method.. 128
Electrolytic Dissociation Measured by the Freezing-point Method..... 129
Improved Freezing-point Method..................................... 130
Results of Measurements of Dissociation by the Freezing-point Method 130
The Three Fundamental Properties of Solutions...................... 132
Freezing of Saturated Solutions.................................... 133

CHAPTER IX

AQUEOUS SOLUTIONS OF ACIDS, BASES, AND SALTS — ELECTROLYTES

What is an Acid?.. 136
What is a Base?... 137
Neutralization of Acids by Bases................................... 137
Importance of this Fact for Chemistry.............................. 139
Heat of Neutralization of Acids and Bases.......................... 139
Exceptions Presented by Weak Acids and Weak Bases 141
Theory of Electrolytic Dissociation as a Correlator of Facts........ 141
Law of the Thermoneutrality of Salts............................... 142
Importance of Energy Changes for Chemistry......................... 143
Color in Solution 144
Absorption of Light Due to Resonance 145
Color in Solution May Be Ionic or Molecular........................ 145
Cause of Color in Solution... 147

Color Changes and Volumetric Analysis — Indicators 148
Stieglitz's Views in Reference to Phenolphthalein 150
Amphoteric Electrolytes — Importance in Living Organisms 151
Amphotenism and Biological Processes 152
Hydrolysis at Ordinary and at High Temperatures 153
Effect of Temperature on Hydrolytic Dissociation 154

CHAPTER X

SOME ELECTRICAL PROPERTIES OF AQUEOUS SOLUTIONS OF ELECTROLYTES

Faraday's First Law 156
Faraday's Second Law 157
Second Law of Faraday and Chemical Valence 157
Nature of Chemical Valence 158
Experiment Demonstrating the Nature of Chemical Valence 159
Electrolytes Conduct Only by Undergoing Electrolysis 161
The Laws of Faraday Apparently Rigid Laws of Nature 163
The Nature of Electrolysis 164
Older Theory 164
The Decomposition Values of the Ions 165
Newer Theory of Electrolysis 166
Newer Theory and Decomposition Values 166
Electrolysis of Water a Direct Decomposition by the Current 170
Property of Solutions of Electrolytes to Conduct the Electric Current 170
The Kohlrausch Method of Measuring Electrical Conductivity 172
Applying the Kohlrausch Conductivity Method 173
Purification of Water 174
Regulation of Temperature 175
Some Results of Conductivity Measurements 176
Law of Kohlrausch and Ostwald 177
Dissociation of Electrolytes Measured by the Conductivity Method 178
Relation between Dissociation and Dilution 179
Conductivity and Dissociation at Elevated Temperatures 181
How Electrolytes are Dissociated by Water 182
Ways in which Ions are Formed 186
Velocities with which the Ions Move 188
Apparatus Designed by the Author 188
Effect of Concentration and Temperature 190
Results of Measurements of the Relative Velocities of the Elementary Ions 191
Interpretation of the Results 192
Absolute Velocities of the Ions 194
Velocities of Ions and of Gaseous Molecules 195
Electromotive Force of Primary Cells 196
Solution-tension of the Metals 197
Proof of the Existence of Solution-Tension 198
Values of the Solution-tension of Certain Metals 198

CHAPTER XI

SOLUTION IN NONAQUEOUS AND IN MIXED SOLVENTS

Solvent Power of Liquids 202
Dissociating Powers of the Different Solvents — Organic Solvents 202
Inorganic Solvents 205
Abnormal Electrolytes 206
Dissociating Power of Solvents and Their Dielectric Constants 209
Determination of the Dielectric Constants of Media 210
Relation between the Dissociating Power of Solvents and their own Association 211
Effect of Rise in Temperature on the Association of Liquids and on Their Dissociating Power 212
Results in Mixed Solvents 212
Mixtures of Water and the Alcohols 213
Mixtures of Acetone with Water and the Alcohols 215
Viscosity and Atomic Volume 217
Dissociation in Nonaqueous Solvents 219
Ternary Mixtures of the Alcohols with Water 220
Glycerol and Mixtures with the Alcohols and Water 221
Rubidium Salts in Mixtures of Acetone and Water 224
Work in Formamide 224
Viscosities of Caesium Salts 225

CHAPTER XII

COLLOIDAL SOLUTIONS

Historical Sketch 226
Work of Graham 227
Diffusion Experiments of Graham 227
Graham's Views on Colloids 229
Work of M. Carey Lea 230
Nomenclature Terms Introduced 231
Nomenclature of Wolfgang Ostwald 233
Methods of Preparing Colloidal Solutions 234
Double Decompositions 234
Reductions 235
Electrical Methods 236
Properties of Colloidal Solutions 237
Osmotic Pressures of Emulsions and of Suspensions 238
Lowering of Freezing-point and of Vapor-tension 239
Diffusion of Colloids 240
Brownian Movement 241
Distance Traveled and Velocities of the Particles 242
Cause of the Brownian Movement 243
Work of Perrin 243
Concentrations of the Colloids at Different Levels 245

Radii of the Particles........ 245
Mass of the Atom 246
The Ultramicroscope........ 247
Principle of the Ultramicroscope........ 247
The Zsigmondy Apparatus........ 248
The Siedentopf Ultramicroscope 249
Nomenclature of Ultramicroscope 249
Results Obtained with the Ultramicroscope. Sizes of the Colloidal Particles........ 249
Motion of Emulsion Particles........ 251
Electrical Properties of Colloids 252
Electrical Endosmosis........ 253
Cataphoresis........ 254
Velocities with which the Particles Move........ 256
Cataphoresis with Emulsoids 256
Electrical Properties of Colloids in Nonaqueous Solvents........ 257
Electrostenolysis........ 258
Conductivity of Suspensions........ 258
Electrical Properties of Emulsions........ 259
Precipitation of Colloids by Electrolytes........ 260
Action of Electrolytes on Colloidal Suspensions........ 261
Microscopic and Ultramicroscopic Observation of the Precipitation of Colloids........ 262
Cause of the Precipitation........ 263
Why a Colloid is Unstable........ 263
How Electrolytes Act 264
Precipitation and the Valency of the Ion with Opposite Charge........ 265
Precipitation of a Positive Sol. 265
Precipitation of a Negative Sol. 266
Precipitation not Proportional to Valence........ 268
Precipitation of Coarser Suspensions by Electrolytes 269
Precipitation of Emulsoids by Electrolytes........ 270
Action of One Colloid on Another 271
Action of Emulsoid on Emulsoid........ 273
Action of Suspensions on Emulsions........ 273
Protective Action of Colloids........ 273
Gels........ 274
Physical Properties of Gels........ 275
Solventation and Desolventation of Gels........ 276
Less Elastic Gels........ 276
More Elastic Gels........ 277
Rate at which Water is Taken up........ 278
Heat Set Free in Imbibition........ 279
Imbibition in Aqueous Solutions........ 280
Theories of Colloids 280
Are Colloids Solutions?........ 280
The Adsorption Theory of Colloids........ 282
The Suspension Theory of Colloids........ 282

Bearing of Colloidal Chemistry on other Branches of Science.......... 283
Bearing of Colloids on Physiological Chemistry.................... 284
Relations between Organic and Inorganic Ferments................. 284
Action of Toxins on Antitoxins................................. 286
Bearing of Colloids on Pharmacology and Pathology................ 287
Bearing of Colloids on Agricultural Chemistry..................... 288
Bearing of Colloids on Mineralogy................................ 289
Colloidal Chemistry and the Chemical Industries.................. 289
Soaps.. 290
Tanning.. 291
Dyeing... 291
Other Technical Applications of Colloids.......................... 293
Adsorption... 294
Nature of the Adsorbent....................................... 294
Effect of Temperature on Adsorption............................ 296
Theories of Adsorption... 297

CHAPTER XIII

SOLUTIONS IN SOLIDS AS SOLVENTS

Solutions of Solids Dissolved in Solids, or Solid Solutions Proper....... 299
Diffusion in Solids... 302
Lowering of the Vapor-tension of Solids by Other Solids............. 303
Lowering of the Freezing-point of a Solid by Another Solid.......... 304

CHAPTER XIV

THE NEWER HYDRATE THEORY

Earlier Work.. 306
Relation between Lowering of the Freezing-point of Water and Water of Crystallization of the Dissolved Substance........................ 307
Approximate Composition of the Hydrates Formed by Various Substances in Solution... 310
Relation between Water of Crystallization and Temperature of Crystallization.. 314
Dissociation as Measured by the Freezing-point Method and by the Conductivity Method.. 315
Temperature Coefficients of Conductivity and Hydration............. 316
Coefficients for Slightly Hydrated Salts........................... 318
Coefficients for Strongly Hydrated Salts........................... 319
Relations between the Coefficients............................... 320
Relation between the Hydration of the Ions and their Ionic Volumes... 322
Hydration of the Ions and the Velocities with which they Move....... 324

CHAPTER XV

THE SOLVATE THEORY OF SOLUTIONS

Hydrate Theory for Aqueous Solutions Becomes the Solvate Theory in Solutions in General 327
Spectroscopic Evidence Bearing on the Solvate Theory of Solution — Work of Uhler 330
"Solvent Bands" — Work of Anderson 332
"Solvent Bands" — Work of Strong 335
Absorption Spectra of Uranium Compounds 335
Absorption Spectra of Neodymium Chloride in Various Solvents 338
Absorption Spectra of Neodymium Nitrate in Different Solvents 339
Transparency of Free and of Combined Water — Work of Guy 341
The Radiomicrometer 342
Solutions more Transparent than pure Water 342
Work of Shaeffer and Paulus 344
Summary of the Lines of Evidence Obtained in this Laboratory, Bearing on the Solvate Theory of Solution 345
How the Present Solvate Theory of Solution Differs from the Older Hydrate Theory 348
Significance of the Solvate Theory of Solution 350
The Solvate Theory and the Theory of Electrolytic Dissociation 351
Does the Solvate Theory Help to Explain any of the Apparent Exceptions to the Theory of Electrolytic Dissociation? 352
Does the Solvate Theory Aid in Explaining the Facts of Chemistry in General, and of Physical Chemistry in Particular? 355
Why the Nature of Solution Is of such Vital Importance not only for Chemistry, but for Science in General 357

INDEX 371

UNIV. OF CALIFORNIA

THE NATURE OF SOLUTION

CHAPTER I

IMPORTANCE OF SOLUTION

The object of this introductory chapter is to call attention to the significance of that condition of matter which we describe as dissolved. We shall see that it is fundamental not only for chemistry, but for many other branches of natural science.

Importance of Solution Early Recognized. — The bearing of solution on natural processes was early recognized. It was clearly seen that without solution there would be no chemistry. This was summarized by the alchemists in the terse generalization, "*Corpora non agunt nisi soluta,*" or in the equally concise, "*Menstrua non agunt nisi fluida.*"

These generalizations are a little too broad in the light of what was known about solutions at the time when they were written. A "solution" in the days of the alchemists was primarily a solution of a solid in a liquid. Even if solution was not limited by them to those systems which result when liquids are brought in contact with solids, this type of solutions was given such a prominence, that it was generally in mind when the term "solution "was used.

Types of Solutions. — The present use of the term "solution" is not only much broader than that adopted by the alchemists, but is far broader than that employed even forty years ago.

We know matter in three states of aggregation — solid, liquid, and gaseous. Matter in every one of these three states can be dissolved in matter of the same state of aggregation as itself and in both of the other states. Thus, we have solutions of gases in gases, or mixtures of gases which do not act chemically upon one another. The characteristic here is unlimited solubility, the properties of the mixture being the sum of the properties of the constituent gases.

Liquids have a vapor-tension in the presence of a gas which is the same as in a vacuum. There is therefore limited solubility of the liquid in the gas.

Solids have a vapor-tension in the presence of a gas which is a function of the temperature.

Solutions of gases, liquids, and solids in liquids are the best and longest known types of solutions.

Gases dissolve in liquids to only a limited extent, the amount, in keeping with Henry's law, increasing with the pressure to which the gas is subjected.

Liquids dissolve in liquids, many of them to an unlimited extent. Liquids which, at ordinary temperatures, have only limited solubility in other liquids, often become infinitely soluble at more elevated temperatures. Solids dissolve in liquids to a limited extent, the amount for any solid being a function of the temperature.

Solutions of gases and liquids in solids are well known. Carbon dioxide dissolves in charcoal, hydrogen in many metals, etc., and a large number of liquids dissolve in many solid substances. One of the newest and most interesting types of solutions is that of solid in solid. Solid solutions came into prominence about twenty-five years ago, when it was shown, as we shall see, that mixtures of certain solids exhibit all of the properties of solutions of liquids or solids in liquids. This will be discussed later at some length under "solid solutions."

We shall use the term solution throughout this book in the broad, modern sense referred to above.

State of Aggregation a Function of Conditions. — The relations between solids, liquids, and gases, are now pretty well understood. Formerly, certain substances were known only in the solid state, others only in the liquid condition, while others still were always gaseous. We now know that the state of aggregation, of elementary substances at least, is primarily a function of the temperature and pressure to which they are subjected, and especially of the temperature — a gas to be liquefied must not be above the critical temperature. Every one of the more common elements is known as a liquid and a gas, and all except helium as a solid. The reason why helium has not been solidified is its very low freezing-point, below −268°, and the comparatively small quantity thus far obtainable.

The history of the liquefaction of the more resistant gases is one of the most fascinating chapters in modern physical chemistry. Of these, oxygen was the first to succumb. This was accomplished by Cailletet,[1] on the one hand, and Pictet,[2] on the other. The former allowed highly compressed oxygen cooled in liquid sulphur dioxide to expand quickly, when some of the oxygen was liquefied. Its boiling point is −184°.

Hydrogen was first liquefied by Wroblewski.[3] He cooled highly compressed hydrogen in liquid oxygen which was boiled under low pressure. The boiling-point of liquid hydrogen is −252°. When liquid hydrogen was evaporated under diminished pressure it froze at −255°.

Compressed helium, when cooled in liquid hydrogen and allowed to expand suddenly, was partly liquefied at −268°. As already stated, helium has not yet been solidified. For details in connection with the liquefaction of gases some work[4] must be consulted which deals especially with this subject. The liquefaction of gases is, then, a completed chapter of science.

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[1] *Compt. Rend.*, **85**, 1217 (1877).

[2] *Ibid.*, **85**, 1214, 1220 (1877).

[3] *Ibid.*, **98**, 149 (1884).

[4] Hardin: *Liquefaction of Gases;* also the Author's *Elements of Physical Chemistry,* 4th edition, pp. 85 to 90. (The Macmillan Co.)

The melting of solids has been facilitated very greatly by the electric furnace. By means of it very high temperatures are obtainable, and under conditions which can be readily worked with.

The question as to whether a compound is a solid, liquid, or gas, is not simply a function of temperature and pressure. Another factor comes into play, and that is the stability of the compound. Many compounds are stable only in the solid form. Others can be liquefied, but cannot be volatilized even under low pressure.

The object of this paragraph is to call attention to the fact that the former conceptions of solids, liquids, and gases have been considerably modified in the light of recent advances; and especially that this is in keeping with the recent developments in connection with our conception of solutions. Formerly, we knew practically only solutions in liquids, as the solvents. Now we know solutions in gases, in liquids, and in solids as solvents. There is perhaps a certain analogy in the developments along these two different lines.

Aqueous Solutions the Most Important. — Solutions in water as the solvent were early recognized as the most important. The old Greek philosophers regarded water as "the beginning of all things." Said Thales, "all things have their origin in water and return unto the same."

The father of medicine, Hippocrates, laid great stress upon the healing power of water, and his successors referred again and again to the same point. Van Helmont, in the seventeenth century, regarded water as the substance of all things. It was the original element into which everything else could be transformed. In the same century Basil Valentine was equally insistent upon the importance of water in chemistry. Said he, "Water is the mother of all the metals."

This brings us to Robert Boyle, who also lived in the seventeenth century. In his book, "Sceptical Chymist," he lays stress upon the earlier view that water is the origin of all things, and adds that "it seems evident that water may be transmuted into all the other elements." "Not only plants, but animals and minerals may be produced out of water." Boyle thus went farther in his laudation of the importance of water than any of his predecessors.

The importance of solution, especially in water as the solvent, was by this time generally recognized. Solution was the fundamental condition. Here all transformations took place.

Under these conditions it was only natural that chemists should look for a *universal solvent* — something which would dissolve everything else.

Paracelsus, in the sixteenth century, termed this universal solvent and healing medium "*alkahest.*" Paracelsus did not describe the physical and chemical properties of alkahest in general. This remained for Van Helmont. It was a liquid substance resembling water, whence its name "*Ignisaqua.*"

The existence of this hypothetical, ideal solvent was soon called in question. In 1675 Lémery regarded it as simply imaginary; and Robert Boyle in his above mentioned work called its existence into question.

Alkahest was a myth, but the conception of a universal solvent led to a large amount of work with solutions, and an extension of knowledge in this field. Like so many other erroneous hypotheses it thus led to important results.

Present Use of the Term Solution. — We recognize today, as did the alchemists, that aqueous solutions are the most important. Water is the most general solvent known to man. Aqueous solutions are the most important in chemistry, and are fundamental, as we shall see, for all biological phenomena.

We use the term solution today, however, in the broad sense in which it has already been defined. Solutions in solvents other than water also play a prominent rôle in chemistry. Solutions in the alcohols and other neutral, organic solvents are important not only in pure chemistry but in the chemical industries as well.

To judge of the importance of that condition of matter known as dissolved, we must use "solution" in the broader and more modern sense. We must consider solutions of gases, of liquids, and of solids in gases, in liquids, and in solids. With this conception in mind let us see what is the bearing of solution on chemistry.

Solution and Chemical Transformation. — We can perhaps best understand the importance of solution for chemistry by recalling the operations of qualitative analysis. Most of the reactions there involved take place in solution, and in aqueous solution at that. We dissolve salts and bring their solutions together in order to have them react. The dry, undissolved solids would not react; their solutions react immediately on contact.

In some cases the reactions are carried out at higher temperatures, and then the salts are fused together. A fused mixture of two or more substances is just as truly a solution as cane sugar in water at ordinary temperatures. The definition of solution as "a homogeneous mixture of two or more substances, the constituents of which cannot be separated mechanically," does not contain any reference to temperature. We have solutions at very low temperatures, at ordinary temperatures, at elevated temperatures, and at very high temperatures. They are all solutions and obey the laws of this condition of matter.

When we want an acid or a base to react, we do not use the pure, homogeneous substance, but we dissolve it in water. As we shall see, no pure acid or base, so-called, has any acid or basic properties. They become acids or bases only when dissolved in water or some other solvent. The reason for this will be pointed out later.

When we wish to analyze any solid, one of the first steps consists in finding a solvent for it — in getting it into solution. Not until it is dissolved do the general methods of analysis apply to it. The reason for this will also become apparent in the proper place.

Solution Fundamental for all Branches of Chemistry. — What has been said in reference to the importance of solution for qualitative chemistry, applies with equal force to other branches of chemistry. Quantitative chemistry is absolutely dependent upon solution both for gravimetric and for volumetric work. Precipitations are, of course, effected in solutions, and in all titrations both the matter titrated and the substances used to titrate are dissolved.

When we turn to organic chemistry we find that the same condition obtains. Reactions here, in general, take place in solution in the broader sense of that term. Aqueous solutions are frequently used, but solutions in solvents other than water — non-aqueous solutions — are also employed.

Certainly in modern physical chemistry solutions are fundamentally important. Indeed, those recent developments in chemistry which are classed under the head of physical chemistry deal largely with the properties of solutions.

As we shall see, it was the partial recognition of the real nature of solution, and of the relation between solutions and gases, which made possible many of these recent developments. Solution is the keystone to chemistry. We might almost say "without solution, no chemistry" — at least no chemistry in the sense in which we now know this large and important branch of natural science.

Dry Substances do not Generally React Chemically. — The bearing of solution on chemistry can perhaps be seen best, if we examine the chemical behavior of substances when out of solution. Take those substances whose aqueous solutions are chemically among the most active, and see how these same substances behave when "dry." Here we are using the term "dry," not meaning simple freedom from water or aqueous vapor, but from all dissociating solvents.

Dry Chlorine and Dry Sodium. — It was shown by Wanklyn[1] that when dry chlorine gas is passed over fused metallic sodium, there is no action. In his own words, "When chlorine gas is passed over metallic sodium — even when the metal is fused and whilst in a state of fusion, shaken in contact with the gas, so as to expose fresh metallic surfaces — there is no action. A glass vessel containing a piece of sodium was weighed, and, after the transmission of chlorine under the circumstances above named, it was re-weighed.

	Grams
Weight before the action of chlorine	7.847
Weight after the action of chlorine	7.863
Gain	0.016

The quantity of metallic sodium taken for the experiment was 0.770 grams."

This explains the result which has so often been obtained upon the lecture table, when chlorine gas was carefully washed and *dried*, and then passed over heated metallic sodium to show the direct union of sodium and chlorine, forming sodium chloride. The fused sodium maintained an untarnished surface in contact with the chlorine gas, until the experimenter, perhaps in disgust, opened the tube containing the fused sodium and the chlorine gas. On opening the tube a little moist air was introduced; enough moisture being added to cause the sodium and chlorine to react with a violence which gave more satisfaction to the observing class of beginners than to the experimenter.

Dry Hydrochloric Acid Gas on Dry Carbonates. — The action of dry, hydrochloric acid gas on Iceland spar and witherite was studied by Hughes.[2] In his own words, "The variations in weight which we observed were so minute that no definite assertion can be made of an action having taken place; and the slight variations observed may be due to experimental errors, and to the imprisonment or entanglement of the molecules of hydrochloric acid gas amongst the finely divided particles of the Iceland spar or witherite."

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[1] *Chem. News*, **20**, 271 (1869).

[2] *Phil. Mag.*, **34**, 117 (1892).

Dry Acids on Dry Litmus. — A still more remarkable experiment was described by Marsh.[1] "An acid to affect blue litmus must be more or less dilute; in other words, water is necessary for the particular action, whatever it may be, which occurs when blue litmus becomes red." "I have found that dry litmus paper in hydrochloric acid dried with phosphorus pentoxide, does not appreciably alter in color for some time. Ordinary concentrated sulphuric acid does not redden litmus paper, but imparts a more or less bluish purple tint to it; and the Nordhausen acid acts similarly."

Dry Ammonium Chloride Sublimes Undecomposed. — More remarkable, however, than any of the above experiments is that carried out by Baker.[2] His paper, "Influence of Moisture on Chemical Change," is one of the most interesting that has ever been written upon this subject. He points out that "dried ammonium chloride may be sublimed from a mixture of the salt with dried lime without ammonia being liberated"; and that "dried ammonium chloride does not dissociate when heated to 350°."

Dry Hydrochloric Acid Gas on Dry Ammonia. — The experiment described in this paper by Baker, upon which it is desired to lay special stress, is the behavior of a mixture of dry hydrochloric acid gas and dry ammonia. Helmholtz and Richartz had noted that no fumes are produced when these gases, previously dried, are brought together; they, however, believed that the chemical action still went on, although the ammonium chloride was not precipitated in the form of powder.

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[1] *Chem. News*, **61**, 2 (1890).

[2] *Journ. Chem. Soc.*, **65**, 611 (1894).

Baker prepared his ammonia by heating purified ammonium chloride with purified lime. He passed the ammonia first over solid potash, and then over a mixture of copper oxide and potassium oxide. The latter was recommended by Stas as being a better drying agent than phosphorus pentoxide. Baker prepared it by fusing finely divided copper with potassium nitrate. The ammonia was then introduced into one arm of the tube [Fig. 1], over phosphorus pentoxide. Ammonia thus prepared had no action on phosphorus pentoxide.

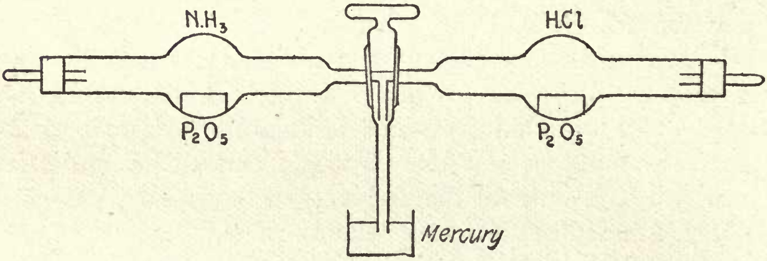

FIG. 1.

The hydrochloric acid gas was prepared by the action of pure sulphuric acid on recrystallized sodium chloride. The gas was introduced into the other arm of the tube, and allowed to stand for a week in contact with phosphorus pentoxide.

When the gases were mixed no white fumes were produced. "On connecting the interior of the tube with dried mercury, by means of the third limb of the tap, the mercury did not rise, showing that no combination of the gases had taken place." "If a trace of moist air be admitted to the mixture of dry gases, dense white fumes are at once produced, and the mercury rushes up into the tube."

Gutmann[1] obtained opposite results from Baker, but Baker[2] repeated his work and showed that Gutmann had not taken the proper precautions in drying the gases. Gutmann used phosphorus pentoxide which probably contained metaphosphoric acid; if so, this was the cause of the different result obtained by him. In his later work, Baker obtained the same result with reference to the inaction of dry ammonia and dry hydrochloric acid gas, and also found that properly dried ammonium chloride when volatilized had a normal molecular weight.

Dry Sulphuric Acid on Dry Metallic Sodium. — A result still more remarkable than any of those already referred to, is the inactivity of dry sulphuric acid on dry metallic sodium. If there is any reaction in all chemistry which we would suppose, on *a priori* ground, must always take place whenever the constituents were brought together, it would be the reaction between metallic sodium and sulphuric acid. From our general knowledge of the substances chemically, it is difficult, not to say impossible, to conceive of them existing in the presence of one another without entering into chemical combination.

The writer has seen the following experiment[3] performed. A piece of metallic sodium which had been dried with special care over phosphorus pentoxide, was immersed in sulphuric acid which had also been dried with very special care. When the sodium first touched the sulphuric acid there was incipient reaction, due to the sodium having taken up on its surface a little moisture in passing through the air during the transfer from one vessel to another. This was over in a moment. The sodium then remained suspended in the sulphuric acid as quietly as if in ligroin.

If one desires to repeat any of the above described experiments, very special precautions must be taken to dry all of the substances involved. The difficulty in removing water from almost anything can be appreciated when we consider that Stas was able to pump water out of a glass tube which had been heated to redness for a month, the

[1] *Lieb. Ann.*, **299**, 267 (1898). [2] *Journ. Chem. Soc.*, **73**, 422 (1898).

[3] *Proceed. Chem. Soc.*, p. 86 (1894).

tube having been attached all the while to a vacuum pump. This shows that the usual methods of drying are entirely inadequate in work such as that which has just been described. The failure to recognize this fact has led certain experimenters to perform some of the above experiments to their sorrow.

What has been stated in reference to the bearing of solution on chemical action could be elaborated and supplemented almost indefinitely. Enough has been given, however, to show that things in the pure, homogeneous condition do not, in general, react chemically. It is only when matter in one state of aggregation is mixed with matter in the same or in a different state of aggregation — is dissolved — that it becomes really active from the chemical standpoint. The melting of a solid or the volatilization of a liquid are not ordinarily considered as chemical reactions.

Dry substances not infrequently react when fused together at elevated temperatures. In such solutions rise in temperature produces an effect, as we shall see, analogous to that of the solvent at ordinary temperatures. This is in no wise opposed to the point which is brought out in the preceding sections. Of chemical reactions in general, relatively few take place out of solution. Solution is therefore absolutely fundamental for chemistry.

Importance of Solution for Physics. — When we turn from chemistry to physics we find solution not playing so prominent a rôle as in chemistry, but still one of importance. The conduction of heat in solutions, the absorption of light by solutions, and the passage of electricity through solutions are important for physics. We may also mention surface-tension, viscosity, diffusion, polarization, electrolysis etc., of solutions; phenomena which have long attracted the attention of physicists. Again, consider the primary and secondary electrical batteries. The primary cells, prior to the invention of the dynamo, were for a long time the chief source of electricity; and primary cells in general depend for their existence upon the solutions of the electrolytes around their poles. Secondary cells are equally dependent upon solutions, and secondary cells are coming more and more into prominence in studying electrical phenomena. These are only a few of the many applications of solutions in physics.

Solution and Geology. — Solution, used in the broad sense already indicated, is of importance in geology. Rocks in general are formed from molten magmas (igneous rocks), or are deposited from aqueous solutions or suspensions in water (sedimentary rocks); the molten magmas being simply solutions of various substances in one another at high temperatures; and whether a system is, or is not, a solution does not raise the question of temperature. As we have seen, we can have solution at any temperature. A molten geological magma at a temperature of several thousand degrees, is as much a solution as alcohol or cane sugar in water at ordinary temperature. Solution is, therefore, fundamental to this branch of geology.

The sedimentary rocks are deposited from aqueous suspensions or aqueous solutions. The solid material is often in a state of purely mechanical suspension in the water. In other cases it is more finely divided, or in a state of colloidal suspension, as it is termed. It may be still more finely divided and exist as a colloidal solution; or it may be in the water as a true solution. In any case the liquid is essential to the formation of the sedimentary rocks. This does not refer to the aeolian or to the glacial rocks.

Minerals crystallize in general either from molten masses or from aqueous solutions — in either case from solution — and mineralogy is an important branch of geology.

Heinrich Rose called attention to a geological action which is now generally recognized, illustrating the important rôle of solution in geology. Carbon dioxide in the air or in the water in the earth, acting through long periods of time, decomposes the silicates. This is an important factor in the "weathering" of the rocks. Geologically, weathering is an important phenomenon. Over the surface of the globe we have the stable silicates being converted into the less stable carbonates — the carbonation of the rocks, and this materially alters the face of the globe.

This action of large amounts of carbon dioxide over long periods of time illustrates a principle which is also of fundamental significance for chemistry. The silicates are among the most stable and insoluble compounds. Carbonic acid — carbon dioxide in water — is one of the weakest acids. Yet this very weak acid, acting in enormous quantities, which is what the above amounts to, is capable of decomposing large amounts of the silicates. This is one of the best examples, at least in nature, of the effect of mass or quantity as conditioning the *magnitude* and even the *direction* of a chemical reaction. After Rose called attention to the wide-reaching significance of this reaction not only for geology, but for chemistry, no one doubted the importance of the rôle played by mass in chemistry. Indeed, this was one of the most important observations made bearing upon the effect of mass, and it played an important part in calling the attention of chemists to the fact that they must take into account not only the *nature* of the reacting substances, but the *relative quantities* which were brought together. It is an important chapter in the history of the development of the law of mass action.[1]

Solution and Biology. — Solution is quite as important for the various branches of biology as it is for chemistry. Take *zoology*. Animals are composed largely of water. If we dessicate almost any animal, it loses more than half its weight, and most animals lose much more than half their weight. Take a human being of average weight, say about one hundred and fifty pounds; when completely desiccated he would weigh about sixty pounds.

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[1] See the Author's *Elements of Physical Chemistry*. 4th edition. (The Macmillan Co.)

More important than the large preponderance of water in animals is its function. Animals, in general, cannot "live" long without water, using the term "live" in the sense of grow and reproduce. An amoeba may be roughly described as a solution of a large number of substances in water, surrounded by a membrane, and what is said of amoeba applies to cells in general, and tissues of animals are made up of cells. Remove the solvent, and the animal either dies or lies dormant, and in the latter case may exhibit the phenomena of "life" again when the removed water is restored to it.

Again, animals obtain most of their food either in solution outside of their body, or the food passes into solution after it is taken into the body. In either case the food is in solution, true or colloidal, or in mechanical suspension in water before it is assimilated by the animal.

Solution is no less important in *physiological botany* than in zoology. Vegetable life depends upon water for its existence. This is readily seen in a gross way by comparing the vegetable life in sections which are well watered, with that of the desert, and even in most deserts there is some water. Plants, like animals, are made up of cells, and plant-cells, like the cells of animals, are mainly aqueous solutions.

Plants as well as animals obtain their food largely in solution in water. This is dissolved from the soil and air and then assimilated by the plant. Solution is thus fundamental to botany.

Among the newest of the biological sciences is *bacteriology*. Without raising the question, which is purely one of definition, as to whether these microscopic organisms belong in the classification animal or plant, let us see what they are.

These relatively simple forms of life are also composed of cells. A bacterium, from our standpoint, may be regarded as a very complex aqueous solution, surrounded by a membrane. These simple forms of life, like the more complex, depend for their existence upon solution. Indeed, they may be said to be primarily solutions existing under certain very special conditions.

We now turn to the science of *pharmacology*. Here again solutions are fundamental. Drugs are taken into the body either in solution, or pass into solution in the juices of the body, which are essentially aqueous solutions, before they are functional; and finally consider *physiological chemistry*. The reactions here are almost as much a matter of solution, true or colloidal, as in any other branch of chemical science.

All in all, we can see from this very brief sketch that water is absolutely essential to life. Its chief rôle in living processes is that of solvent. Aqueous solutions are, then, absolutely essential to life. We often say "without carbon, no life." We could just as truly state "without water, no life," at least in its normal condition.

Water a Remarkable Compound. — We are so familiar with water that we are liable to look upon it as a compound of relatively little significance. It is formed in such a large percentage of chemical reactions, and we express it in so many of our chemical equations, that we are in danger of losing sight of, or never thinking of, its importance.

Having seen a little of the fundamental significance of aqueous solutions for chemistry, physics, geology, and biology, perhaps it would not be too great a digression to consider very briefly a few of the more striking peculiarities presented by water itself.

In the first place its composition is remarkable. It is composed of the two most important elements — oxygen and hydrogen. These are the two elements which are required for the formation of acids and bases. The constituent of all acids — that which gives us acidity, is hydrogen, under a certain condition, as we shall see, *i.e.*, carrying a positive charge of electricity. The characteristic constituent of bases is one hydrogen atom united with one oxygen atom, forming what is known as the hydroxyl group and this group carrying one negative charge of electricity, as we shall also see. Water is formed by the union of the hydroxyl of the base with the hydrogen of the acid and acids and bases are of the utmost importance in our study of chemistry.

In addition to the neutralization of acids by bases, think of how many reactions there are in chemistry in which water is formed. One of the substances contains hydrogen and the other hydroxyl, and when they are brought together water is formed and the reaction takes place. This is true especially of compounds of carbon. It is safe to say that a very large percentage of all the chemical reactions known, take place on account of the formation of water when the reacting substances are brought together, and it will be shown that whenever electrically charged hydrogen and hydroxyl are brought together in appreciable quantities, they combine. This shows the importance of the water in effecting so many of our chemical reactions.

Heat Evolved in the Formation of Water. — When water is formed by the union of hydrogen with oxygen, we have the most exothermic or heat-evolving chemical reaction known. When hydrogen and oxygen combine they liberate more heat, per equivalent quantities, than any other reaction in the whole field of chemistry. The resulting compound — water — is one of the most stable of chemical compounds, just as we would expect it to be. Those compounds formed with the largest heat evolution, other things being equal, are the most stable.

Physical Properties. — Given the compound, water, its physical properties are in general *extreme* — their numerical expressions are either extremely large or extremely small, and usually extremely large. Its specific heat is among the largest for any liquid substance. It is the best solvent of all known liquids. It has the highest dielectric constant or specific inductive capacity of any of the more common liquids. This means that two electrical charges separated by water have a smaller attraction for one another than when separated by any of the other common liquids.

As we shall see, the power of liquid solvents to break molecules of acids, bases, and salts down into charged parts or ions as they are termed, is nearly proportional to the dielectric constants of the liquids. Water, of all the common liquid solvents, should therefore be the best dissociant, and such is the fact.

One other property of water, on account of its importance in the economy of nature, calls for special comment. When most liquids are cooled they contract until their freezing-point is reached, when they begin to solidify. Not so with water. It contracts to a temperature of 4° C. and then, with further cooling, expands until its freezing-point is reached. A few other liquids are known which behave in a similar manner. This may seem to be an accidental property of water and of no very great significance; but a moment's thought will show that such is not the case. Did water contract until it froze, the order and economy of nature would in a short time be greatly changed. The fact that water expands from 4° C. to 0° is the cause of water freezing first on the surface and not at the bottom. Did water freeze first on the bottom of our rivers, lakes, and larger bodies of water, fresh water life in our northern climates would soon be exterminated. Those forms of life which depend for food upon these fresh water forms, would be compelled to migrate or would die, and thus the present distribution or equilibrium between the various living forms would be destroyed. This would, of course, seriously disturb the existing order of things.

These are a few, and a very few of the unique properties of water. To discuss them at all fully would require a separate volume. They suffice, however, to illustrate the point that water is not only a remarkable substance, but, all things considered, it is by far the most remarkable and important chemical compound known to man.

Importance of Solution Justifies the Work Expended upon It. — There are few, if any, subjects in chemistry upon which so much work and thought have been expended, especially in recent times, as upon the nature of solution. The reason for this ought now to be apparent. In order that matter should react chemically it must be dissolved. Matter in the pure homogeneous condition, as we have seen, is comparatively inert. Chemistry depends for its existence upon solution. The physical, geological, and biological action of solutions is closely connected with the chemistry of solution.

In solution we are dealing, then, not only with a fundamental condition of matter, but with *the fundamental condition*. This is why so much stress has been laid upon solution in the past, and interest in its nature will probably continue as long as the natural sciences are studied.

CHAPTER II

EARLIER VIEWS AS TO THE NATURE OF SOLUTION

THE views of the Greek philosophers as to the nature of matter in general, and solution in particular, can be learned from a history of chemistry dealing with that period. Much of it is very indefinite and therefore does not vitally concern us today.

A good part of the speculation of the earlier alchemists had to do with the *modus operandi* of solution, rather than with the nature of solution itself. There were those who held that the dissolved particles simply went into the interstices between the molecules of the solvent, and those who thought that there was some kind of a union between the solvent and the dissolved substance.

Isaac Newton. — It was Newton who, in the seventeenth century, discovered the law of gravitation, that matter attracts matter inversely as the square of the distance, and directly proportional to the product of the masses. This was found to apply to matter at great distances apart, and it was only natural that he should attempt to apply it or some other force to matter removed from other matter only an infinitesimal distance, as is the case with the atoms. We had what we might term the gravitational theory of chemical action.

Newton extended this conception also to solution. He observed that when a solid is dissolved in a liquid which is much lighter than the solid, the heavier solid does not settle to the bottom of the containing vessel, but distributes itself throughout the entire volume of the solvent. He asked "does not this indicate that the dissolved parts endeavor to expand themselves and get as far asunder as the quantity of water in which they float will allow?

And does not this endeavor imply that they have a repulsive force by which they fly from one another, or at least, that *they attract the water more strongly than they do one another*."[1]

This discovery of Newton marked a new epoch in dealing with solutions. The solute dissolved in the solvent because of an *attraction* between the two.

Boerhaave. — The view of Newton was somewhat modified and very greatly elaborated by Boerhaave.[2] "It follows from the nature of a solvent, that if it acts on a substance dissolving it, in a similar manner the substance dissolves the solvent. The particles of the solvent and those of the dissolved substance unite, after solution, to form a new, homogeneous substance." . . . "The cause of this must be sought for in both the solvent and the dissolved substance. It is common to them both and acts reciprocally in both."

All that was then known of the action of a solvent, was that its parts unite with those of the dissolved substance. "We are not dealing here with mechanical action, or with violent repulsion or enmity, but rather with friendliness, if we can apply this term to a tendency to union." "*Particulae solventes et solutae . . . se affinitate suae naturae colligant in corpora homogenea.*"

"The changes which the solvent brings about in the dissolved substance appear to be due to the intimate union between the smallest particles of the solvent and of the dissolved substance."

Thus Newton and Boerhaave placed the whole subject of solution upon a new basis. Instead of speculating about the shapes and disposition of the dissolved particles, they attempted to answer the far more fundamental questions, what is the cause of solution and what is its nature?

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[1] See Walden: *Die Lösungstheorien in ihrer geschichtlichen Aufeinanderfolge*, p. 33.

[2] *Ibid.*, p. 33, from H. Boerhaave: *Elementa Chemia.*

Their answer pointed out the analogy between solution and chemical action, in that both consisted in chemical union. They did more than this, in calling attention to the wide-reaching significance of solution for chemistry. The result was that a little later we find Morveau asserting that "chemistry is primarily the science of solutions."

Wallerius. — The next advance in the study of solution we owe to Wallerius,[1] who raised the question, What is the cause, or what are the causes of solution? Among these he enumerated the following:

There must be a similarity between the solvent and solute. Due to this similarity there is an attractive force between the parts, which is greater the more closely the parts resemble one another. Due to this attractive force the solvent and solute unite with one another.

If we omit the first named cause, *i.e.*, the similarity between solvent and solute, we find these suggestions of Wallerius very important. While he was not the first to point out the existence of an attraction or an affinity between solvent and solute, he laid much stress upon it and pointed out the result of its action — combination between the two. He also called attention to the fact that chemical combination is due to an *attraction* or *affinity* between the reacting substances, which is, of course, a matter of fundamental importance.

This brings us, in the study of solution, down to the end of the eighteenth and the beginning of the nineteenth century.

Lavoisier. — The distinguished French chemist, Lavoisier, in 1789, in his "Traité Élémentaire de Chimie,"[2] made an important contribution at least to the classification of solutions. "In *solutions* of salts the salt molecules are simply torn apart from one another, neither the salt nor the water suffering any decomposition. Both can be recovered in the same quantity as before the operation. The same can be said of the solution of the resins in alcohol and in the spirituous solvents. On the other hand, in the dissolution of the metals there is always a decomposition either of the acid or of the water. The metal becomes oxidized, passing into the state of oxide; a gaseous substance is given off — none of the substances after dissolution are in the same state as before."

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[1] *Physische Chemie.*

[2] See Walden: *Die Lösungstheorien in ihrer geschichtlichen Aufeinanderfolge,* p. 47.

Lavoisier thus distinguished clearly between what he called *solution* and *dissolution;* the former being more nearly what we usually understand by the term solution, the latter involving a chemical act. A solution, according to Lavoisier, is a *mechanical mixture.*

Fourcroy. — When we enter the nineteenth century, we find Fourcroy[1] also regarding solution as physical, the dissolved substance being simply in a state of fine mechanical division in the solvent.

Klaproth. — Klaproth[2] considered solution as the result of the action of *chemical affinity* between the solvent and the dissolved substance. This means that there is a reciprocal attraction between the particles of the solute and those of the solvent; and this attraction must be stronger than that of the solute particles for one another, or the solvent particles for one another. As he says, this attraction between the particles of the solute and solvent must be stronger than their "cohesion."

We now come to the contribution to our knowledge of solution by one of the greatest French chemists of the beginning of the nineteenth century — Berthollet.

Berthollet. — His views were expressed in his great book, "Essai de Statique Chimique," — the same work in which the effect of mass on chemistry was first so clearly pointed out. He also called attention to the fact that solution is due to a force which must be great enough to overcome the cohesion of the dissolved substance.

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[1] *Système des Connaissances Chimiques.*

[2] *Systematisches Handbuch der gesamten Chemie.*

Stable compounds were called by Berthollet, "Combinations," the less stable "Dissolutions." Solution is a true chemical combination; the difference between a solution and a chemical compound is to be found in the firmness of the union of the parts. In a solution the parts are less firmly united and the characteristic properties of dissolved substances have not been lost. Chemical union and solution must therefore follow the same laws.

Berthollet, as is well known, did not believe in the laws of definite and multiple proportions in chemistry. To quote his own words from this same book,[1] "Chemists maintain that in compounds they have found between the constituents definite relations, and have often regarded it as a general property of compounds that they can be found only in these unalterable relations." . . . "This assumption rests merely on distinguishing between *solution* and *combination*, thereby confusing the properties which separate the two with affinity which effects combination."

As is well known, this is what led to the historical discussion between Berthollet and Proust, which extended over several years. Berthollet held the view that the law of definite proportions is not true, Proust maintaining that it is. Berthollet was wrong and Proust was right — the laws of definite and multiple proportions are fundamental laws of chemistry.

Berthollet summarizes his conception of solution as follows: "The solvent represents a degree of chemical activity which differs only in degree from that which produces the most stable compound." Solution is thus a purely *chemical* action between solvent and dissolved substance, resulting in the formation of a real chemical compound.

It is interesting to note, that of the two leading French chemists of the beginning of the nineteenth century, the one, Lavoisier, held a purely mechanical conception of solution; the other, Berthollet, a purely chemical.

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[1] See Walden: *Die Lösungstheorien in ihrer geschichtlichen Aufeinanderfolge*, p. 53.

After it was shown that the laws of definite and multiple proportions really hold, it seemed that we must make some distinction between chemical combination, which always takes place in certain definite proportions, and solution which occurs in any proportion, at least up to a certain limit. This was done by Gay-Lussac. He did so by assuming that the force which leads to chemical combination is more powerful than that which produces solution. Still we have a purely chemical theory of solution.

Thomson. — The laws of definite and multiple proportions had been discovered, and Dalton had proposed his atomic theory. This was clearly enunciated by Thomson in his frequently cited "System of Chemistry." Thomson also regarded solution as a chemical process, but distinguished between two kinds of solutions: Solids combine with some of the solvent and remain solid — form hydrates; solids dissolve in liquids becoming themselves liquid. The latter systems are the more strictly termed solutions.

In the first decades of the nineteenth century, men of science took up the quantitative study of solutions. They determined what substances are soluble in various solvents, and the degree of their solubility. They investigated the physical properties of solutions, and then turned to the study of the behavior of solutions when various forms of energy were passed through them. They measured the conductivity of solutions for heat, for light, and for electricity.

Grotthuss. — A name well known in the development of the theories of electrolysis is that of Grotthuss. He regarded chemical phenomena as the results of the phenomena of galvanic electricity.[1] "A galvanism manifests itself in a liquid due to the heterogeneous elementary parts contained in it. No chemical action manifests itself when the electrical forces are in equilibrium. When the equilibrium is destroyed chemical action takes place." Grotthuss recognized that elementary substances can be liquid, and the parts of these were supposed not to be homogeneous. Here was an apparent discrepancy. Grotthuss assumed that since elementary substances which apparently contain no heterogeneous parts are liquid, the elements need not be regarded as made up of simple atoms, but the metals can be regarded as containing at least *positively* and *negatively charged parts,* which are chemically combined with one another.

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[1] See Ostwald's *Klassikern,* No. 152.

The view suggested by Grotthuss, in 1808, is very interesting in the light of the recent work of Thomson.[1] He has electrolyzed hydrogen and has shown that it contains positively charged hydrogen atoms and negatively charged hydrogen atoms. Since the hydrogen molecules are neutral, they are probably composed each of a positive atom and a negative atom which, when united, would give a neutral molecule. Thus, the result found by Thomson was predicted nearly a century before it was experimentally established. In reference to solution proper Grotthuss expresses himself thus: "The solution of a salt in water appears to be only an interpolation of its own elementary parts in the active galvanic molecular circle of water, as the elements of the salt contribute to the galvanic molecular activity of the water. Salts which cannot do this we call insoluble."

Grotthuss also distinguished between "solution" and "dissolution," but used these terms in a somewhat different sense from that with which we have become familiar. "Solution and dissolution are, according to my views, different in this; the former is the conversion by a liquid of a solid into a liquid, where the newly formed liquid product is not separable by galvanic electricity into the original liquid and solid, (*e.g.*, salt dissolved in water); the latter, on the contrary, is the conversion by a liquid of a solid into a liquid, the new liquid product being decomposable by galvanic electricity into its elements (*e.g.*, acids and bases)."

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[1] *Nature*, **52**, 451 (1895).

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We must not confuse these views of Grotthuss, expressed in 1818, with his ideas announced about ten years earlier, which are the basis of his well-known theory of electrolysis. He earlier maintained that in a liquid like water the hydrogen atoms and oxygen atoms are *firmly* and *fixedly* united. A hydrogen atom once combined with a given oxygen atom is always combined with that same oxygen atom. It becomes separated from it only when the current is passed through the solution. More of this when the theories of electrolysis are discussed. His later views which we are now considering are almost exactly the opposite of this. The dissolved particles are continually changing partners. In a salt like potassium bromide, the potassium which at one moment is combined with any given bromine atom, the next moment is combined with a different bromine atom, this exchange of parts going on continually. The relation of these conceptions to the theory of electrolytic dissociation will become apparent when we come to the consideration of that theory.

Berzelius' Electrochemical Theory. — This brings us to the electrochemical theory of the great Swedish chemist, Berzelius. His electrochemical theory must be briefly discussed in order that we may understand his views in reference to the nature of solution.

That there is an intimate relation between electrical action and chemical action was rapidly being recognized by men of science. The primary cell had been discovered by the Galvanis and by Volta. In this cell there was apparently chemical action, and electricity resulted.

Davy had constructed his enormous voltaic pile, consisting of some four hundred couples, and had plunged the poles of this pile apparently into about everything which he could find, to see what would happen. He had studied the electrolysis of aqueous solutions of acids, bases, and salts. He had decomposed fused sodium and potassium hydroxides by means of the current, and had obtained metallic sodium and metallic potassium.

Chemical action produced electricity. The resulting electricity decomposed chemical compounds. This would indicate that there is some close relation between the force that holds together the constituents of chemical compounds, and electricity.

Berzelius, impressed with this idea, developed his electrochemical theory. All atoms are charged both positively and negatively, but there is always a preponderance of one or the other kind of electricity upon every atom, so that we can say that any given atom is charged either positively or negatively. A positive atom and a negative atom are drawn together by the electrostatic attraction of their opposite charges, and they combine and form a chemical compound. Chemical action in terms of this theory is, then, nothing but the *electrostatic attraction of oppositely charged parts.*

The consequences of this *electrical* theory of chemical action are very interesting. If chemical combination is nothing but the result of electrostatic attraction, the properties of the resulting compounds must be a function of the nature of the electrical charges on the atoms in the compound. This is a necessary consequence of the electrochemical theory of Berzelius.

Facts were soon discovered which seemed to militate against this theory. Trichloracetic acid has properties which resemble closely those of acetic acid. Trichloracetic acid contains three chlorine atoms instead of three hydrogen atoms, and the chlorine atoms were supposed to be charged negatively. If this were a fact it would be difficult to explain in terms of the Berzelius theory. The electrical condition of the compound is changed without changing its general properties. It is well known that J. J. Thomson[1] has shown comparatively recently that the chlorine atoms in trichloracetic acid are charged positively like the hydrogen atoms which they replace, and the above-mentioned fact is now in perfect accord with the Berzelius theory.

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[1] *Nature,* **52,** 452 (1895) and Author's *Elements of Physical Chemistry,* 4th edition, p. 362. (The Macmillan Co.)

We recognize today that the Berzelius theory contains a large element of truth.

Berzelius' Theory of Solution. — Having in mind Berzelius' theory of chemical action, we can now understand his views as to the nature of solution. Solution differs from chemical action in that it takes place without any electrical act. A dissolved substance is more active chemically than the same substance when not in solution, and it must, therefore, preserve the electrical difference of its parts.

Berzelius regarded solution as due to some unknown modification of affinity, which gave a very different result from the action of affinity itself. Solution he regarded as essentially a mechanical process.

"The kind of force which effects the solution of a solid in a liquid is not identical with the force which brings about chemical union, and is not to be confused with it. When the latter acts heat is formed, while the force which produces solution absorbs heat and lowers the temperature."[1]

This is a rather sharp distinction, and, considering the time when it was suggested, has a peculiar interest of its own.

Berzelius, of course, knew that heat is often evolved in processes of solution. He accounted for this as due to the dissolved substance; and this evolution of heat could readily be larger than the heat absorption due to the process of solution. Dissolved substances do not alter their chemical properties, they simply alter their state of aggregation, and become chemically more active due to the fact that they are dissolved. One fundamental difference between solutions and chemical compounds had been noted by several, including Berzelius. Chemical compounds are formed in terms of the law of definite proportions. Solution takes place in any quantity, up to a certain maximum limit. This, as we now know, is a fundamental difference. This brings us to the views of Gay-Lussac.

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[1] *Lehrbuch der Chemie* I (1842).

Gay-Lussac. — The rôle played by Gay-Lussac in the development of our knowledge of solution is historically not only of interest, but very important. He seems to have been the first to recognize clearly a *relation between solutions and gases*. In his own words,[1] "Like the elasticity of vapors, the solution of a substance varies with the temperature. It is without doubt also dependent on the reciprocal affinity of solute and solvent; but since the effects of affinity are not variable with temperature, while those of solution depend fundamentally upon it, it would be difficult not to admit that in solution, as in vaporization, the product is essentially limited for each degree of temperature by the number of molecules which can exist in a given portion of the solvent. For the same reason that the elastic molecules are precipitated by lowering the temperature, they are separated, and probably also, like the latter, by the compression and reduction of the volume of the solvent."

We now come to the important point in the paper by Gay-Lussac.[2]

"Solution is, then, fundamentally related to vaporization in the sense that both are dependent on temperature and obey its variations. Therefore, there ought to be between the two, if not a complete identity of result, at least a close analogy; their essential difference consisting in this, that the gaseous molecules do not need a solvent to maintain them in a given space. Their repulsive force is sufficient for this purpose. On the other hand, in a solution of a solid or a liquid, the molecules are not able to maintain themselves in the space, if they are not united by affinity to the molecules of the solvent.

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[1] *Ann. Chim. Phys.* [2], **70**, 424 (1839).

[2] *Ibid.*, 425.

"The analogies between solution and vaporization extend also to the effects on them of variation in temperature; and as it appears to me unquestionable that the elastic force of the vapor of a substance is independent of the state of this substance and of the cohesion of its molecules, since the one remains constant while the other varies, from analogy I am inclined to admit that solution is equally independent of cohesion.

"However, admitting the analogies between vaporization and solution, we must ask why it is, that, while the elastic force of vapors obeys a regular law, increasing regularly with the temperature, the solubility of certain salts shows a maximum and then decreases."

This, Gay-Lussac explains as due to a change in the composition of the compound at the temperature in question.

These views of Gay-Lussac are very important, in that they are the forerunner of quantitative relations between solutions and gases, pointed out nearly a half century later by Van't Hoff, which, as we shall see, are by far the most important contributions to our knowledge of solutions that have thus far been made.

Gay-Lussac first called attention to the *analogy between matter in the gaseous and in the dissolved states.*

There were quite a number of prominent men of science of this period who advocated a chemical theory of solution, *i.e.*, that solution is due to a force acting between the solvent and the dissolved substance which caused the two to combine.

Williamson. — The English chemist, Williamson, published a paper in 1851, "On the Theory of Ether Formation,"[1] which has proved to have great value in more directions than one. Its greatest service has probably been in pointing out the real nature of chemical equilibrium — that it is not a statical condition as had been hitherto supposed, but a dynamical one, representing that condition where the two opposite reactions have equal velocities.

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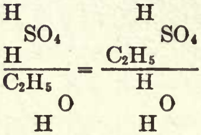
[1] *Lieb. Ann.*, **77**, 37 (1851).

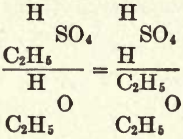
This paper is also of interest and importance in its bearing on the development of the theory of solution, and in this connection must now be considered. Williamson pictured the action of sulphuric acid on ethyl alcohol as follows:



$$\begin{array}{l} H \\ \quad SO_4 \\ H \\ \hline C_2H_5 \\ \quad O \\ H \end{array} = \begin{array}{l} H \\ \quad SO_4 \\ C_2H_5 \\ \hline H \\ \quad O \\ H \end{array}$$

This means that when sulphuric acid reacts with ethyl alcohol, there are formed ethyl sulphuric acid and water.

When, however, more ethyl alcohol is allowed to react with ethyl sulphuric acid, the reaction, according to Williamson, takes place in the sense of the following equation:



$$\begin{array}{l} H \\ \quad SO_4 \\ C_2H_5 \\ \hline H \\ \quad O \\ C_2H_5 \end{array} = \begin{array}{l} H \\ \quad SO_4 \\ H \\ \hline C_2H_5 \\ \quad O \\ C_2H_5 \end{array}$$

In this part of the reaction sulphuric acid and ether are formed.

In the first part of the reaction, as will be seen, the hydrogen of the sulphuric acid is replaced by the ethyl group. In the second stage the ethyl group of the ethyl sulphuric acid is replaced by hydrogen — the one reaction being, in a sense, just the reverse of the other.

Williamson would explain these and similar facts in the following manner, to quote his own words:[1] "We are thus led to the assumption that in a number of molecules of any compound, a continual exchange is going on between the elements in the compound. Let us take, for example, a vessel containing hydrochloric acid; it is filled with a large number of molecules of HCl. The above considerations would lead us to the assumption that an atom of hydrogen does not remain quietly attached to the atom of chlorine with which it was first combined, but there is going on a continued exchange of place with other hydrogen atoms. This change is for us, of course, not directly detectable, because one atom of hydrochloric acid is just like another."

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[1] *Lieb. Ann.*, **77**, 46 (1851).

This view, that in solution there is a constant interchange of parts, implies that in solution things are more or less broken down into their parts. Indeed, Williamson went farther than was necessitated by the facts, and assumed more decomposition in solution than was necessary, as was shown by subsequent work.

Clausius. — The physicist Clausius, in 1856, published a paper,[1] "On the Conduction of Electricity in Electrolytes," which proved to be of very great importance. In this paper Clausius criticizes Williamson for having gone too far, indeed, much farther than the facts required or justified.[2] "Williamson appears to have assumed a greater interchangeability in the grouping of the part molecules than is necessary to explain the conduction of electricity. He speaks of one hydrogen atom continually changing places with another, while to account for the conduction of electricity, it is sufficient to assume that as the whole molecules strike against one another, there occurs, perhaps relatively seldom, an exchange of the part molecules."

Clausius then proceeded to develop his own theory. If we assume that an electric current is necessary to decompose the whole molecules into part molecules, then the force necessary to break down these whole molecules must have a certain value. If this force were not applied, *i.e.*, if the force were smaller than that necessary to decompose the molecules, no current would pass and no electrolysis would take place. As the force is increased until it reaches the decomposition value, there would be no decomposition until this value is reached; then, suddenly a large number of molecules would be decomposed by the current.

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[1] *Pogg. Ann.*, **101**, 338 (1856).

[2] *Ibid.*, 353.

The facts are directly opposed to this conclusion. It had been shown[1] that an infinitesimal force is capable of effecting a corresponding electrolysis of water; and the amount of the electrolysis is proportional to the force acting upon it. A force altogether too small to decompose even one molecule of water can electrolyze water. The conclusion from this fact is obvious. If a force too weak to decompose water can electrolyze it, the current must find the water already decomposed, at least to some extent.

Clausius' theory of the nature of solutions of electrolytes is, then, as follows: Such a solution consists chiefly of "whole molecules," as they were termed, but there are also present a few "part molecules." The whole molecules are breaking down and the part molecules recombining all the time.

When an electromotive force is impressed upon such a solution, the current does not have to break down the molecules of the electrolyte. It finds some of them (part molecules) already in a state of decomposition. The current exerts only a *directing action*, driving the positively charged parts in the direction of the negative pole, and the negatively charged parts in the direction of the positive pole.

We can now understand in terms of the theory of Clausius, how a current too weak to decompose even one molecule of water can effect the electrolysis of water. It is not necessary to decompose the water. The current finds the water already slightly decomposed into "part molecules." It is only necessary for the current to exert a directing action on these parts, and electrolysis is the result. The historical importance of the theory of Clausius will be seen when we come to consider the theory of electrolytic dissociation.

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[1] See Author's *Elements of Physical Chemistry*. 4th edition, p. 368 (Macmillan Co.).

Kopp. — Kopp distinguished between compounds which obey the law of definite proportions, and those in which the constituents are present in varying proportion. The latter are, in general, solutions. Kopp defines a solution of a salt in water as, "a compound, the constituents of which are present in varying quantities." A concentrated solution is an unstable compound of the dissolved substance with water. The composition of this compound can be easily varied by change in temperature, and by many other means.

Kopp points out one marked difference between the properties of stable or well-defined chemical compounds and solutions. When substances unite and form a definite, stable compound, most of the properties of the compound are very different from those of its constituents. Indeed, we know today that about the only property of the constituents which persists in chemical action is mass. To within the limit of accuracy of our most refined chemical balance there is no change in mass in chemical reaction.[1]

The properties of solutions, on the other hand, are often additive, if they are the sum of the properties of the constituents. The properties of other solutions are the mean of the properties of the several constituents. In still other solutions the properties of one constituent affect those of the other constituents to a greater or less extent. In these cases the properties of the solution lie somewhere between those of the several constituents. This is an important distinction between true, stable, chemical compounds, and the more unstable hydrates which, as we shall see, exist so often in aqueous solution.

Guldberg and Waage. — The landmarks in the history of any branch of science are the generalizations or laws that have been reached correlating the phenomena in question. The highest aim of the man of science is to discover such a law.

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[1] Landolt: *Zeit. phys. Chem.*, **12**, 1 (1893); **55**, 589 (1906).

Two names which will always live in the history of chemistry, because the men discovered not only a law of chemical action, but one of the most wide reaching and important laws of all chemistry, *viz.*, the law of mass action, are those of the Norwegian physicist, Guldberg, and the Norwegian chemist, Waage.

These men have a place also in the history of the development of our present conception of the nature of solution. They recognized in general the two classes of chemical compounds, those in which the constituents are present in definite relations, and those in which they are not. They also recognized the existence of compounds intermediate between the above two classes. These are present in solution. Indeed, there are all gradations from compounds obeying rigidly the law of definite proportions to those which do not conform at all to this law. All of these substances are produced by the action of the same force.

The distinctively new feature introduced by Guldberg and Waage, in connection with solution, is that in solution the molecules of the dissolved substance are not free from one another, but they are united in larger or smaller groups, and the size of these groups varies with the temperature of the solution, and probably also with the dilution.

The "groups" of Guldberg and Waage are, of course, groups of the same kind of molecules. They are what we today call polymerized molecules.

Valson. — In 1870 a very important contribution to our knowledge of solutions was made by Valson.[1] From the study of the capillary action of liquids, Valson discovered what he termed the "law of capillary moduli." This he describes in the following words.[2] "Let us call a salt Mm: M being the metallic radical, and m, the non-metallic. If now we pass to a second salt Mm', containing the same metal united with a different non-metal, the capillary effect due to the radical M remains constant whatever the nature of m. Similarly, if we pass from the salt Mm to a salt $M'm$, the capillary effect due to the radical m will be the same whatever the nature of the metal. Finally, if we pass from the salt Mm to a salt $M'm'$, in which both radicals have at the same time been changed, the total effect would be equal to the sum of the effects produced by the two radicals taken separately; provided the solutions are sufficiently dilute and are moreover in a state of normal solution, *i.e.*, that they contain one equivalent of the salt dissolved in one liter of water.

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[1] *Ann. Chim. Phys.* [4], **20**, 361 (1870).

[2] *Ibid.*, 364.

"I give to this effect the name *capillary modulus*, and I am able to enunciate the following law, which holds for saline solutions.

1st. "The modulus of a metallic radical is constant and independent of the non-metallic radical with which it is associated.

2nd. "The modulus of a non-metallic radical is constant, and independent of the metallic radical with which it is associated.

"If the two radicals change at the same time, the modulus is equal to the sum of the two partial moduli.

"The modulus of a salt is equal to the sum of the moduli of its two radicals."[1]

Valson found that these relations held only for fairly dilute solutions.

"The determinations of the moduli were made in solutions containing one equivalent of salt dissolved in one liter of water. It might at first seem better to use more concentrated solutions containing, for example, two equivalents of salt" . . . "On comparing dilute solutions, experiment shows that the capillary effects are approximately proportional to the quantities of the substances used; but this is not the case for concentrated solutions, where the actions of the molecules are not independent of one another. It thus seems that in order that the saline molecules may be regarded as having acquired a state of freedom, it is necessary that they be in a sufficiently dilute solution."[1]

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[1] *Ann. Chim. Phys.* [4], **20**, 386 (1870).

Thus was pointed out clearly the difference between dilute and concentrated solutions. The additive properties which were found in dilute solutions did not hold in concentrated. We shall see that this distinction between dilute and concentrated solutions is one of fundamental importance, the meaning of which has been only comparatively recently pointed out.

Valson showed later that the specific gravities of solutions of salts conform to the same general relations as their refractivities — for dilute solutions they are additive.

Favre and Valson. — Favre and Valson,[2] in their paper on the relation between thermal effects and contraction in solution, showed that what they termed "moduli of coersion" were analogous to moduli of thermal effects, density and capillarity.

"Do[3] not the results in the last table lead us to ask whether the solvent action of water on salts is not to dissociate them into their elements, and to place them, if not in a state of complete freedom, at least in a state of reciprocal independence, which it would be difficult at present to define, but which is very different from their original state.

"This independence of the saline elements on standing is not simply an hypothesis. It is a conclusion to which we have repeatedly been led in the course of our researches. Without going into details we shall content ourselves with recalling what we have said in general on thermoneutrality, on moduli of density and capillary action, and finally, on the moduli of coersion. . . . In sufficiently dilute solutions of salts, each of the metallic or non-metallic elements of the salts always produces the same effects, and these are independent of the other elements which are present."

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[1] *Ann. Chim. Phys.* [4], **20**, 386, (1870).

[2] *Compt. Rend.*, **75**, 330, 798, 925, 1000 (1872).

[3] *Ibid.*, pp. 1004 and 1005.

Favre and Valson then draw the following conclusion: "Solution gives to the elements of the dissolved substance a reciprocal independence, and the inner mechanical work necessary to produce this effect is measured by the changes in volume which accompany solution and, consequently, by the quantity of heat set free when the same effects of coersion are produced directly on the solvent liquid."

When we come to consider the theory of electrolytic dissociation, we shall see that the work and conclusions of Favre and Valson bear directly upon it. Had they regarded the salt parts as charged when dissociated from one another, and had they pointed out a method for measuring the magnitude of the dissociation, they would have approached very closely to the theory of electrolytic dissociation.

As we shall see, however, the discovery of this epoch-making generalization was left for another.

Landolt. — A large amount of work was done at this time which brought out the additive properties of aqueous solutions of salts. Landolt[1] studied the power of substances to rotate the beam of polarized light, and found for such substances as tartaric acid and its salts that the rotation is independent of the optically inactive constituent present. This would indicate that in solution the molecule is broken down into its constituents.

Gladstone. — From his work on the refractivity of solutions, Gladstone[2] had earlier shown that the refractive power of a salt is the sum of two constants, the one depending for its value upon the metal, and the other upon the non-metallic constituent present.

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[1] *Ber. d. chem. Gesell.*, 6, 1073 (1873).

[2] *Phil. Mag.*, **36**, 313 (1868).

Kohlrausch. — Friedrich Kohlrausch[1] had worked out his well-known method for measuring the conductivity of solutions of acids, bases, and salts, and had studied the power of these solutions to conduct the electric current. He had discovered the law, which bears his name, of the independent migration velocity of the ions. This says that the conductivity of any solution, referred to molecular quantities of the dissolved substance — the molecular conductivity — is the sum of two constants, the one depending for its value on the cation, the other on the anion.

These and many other results which were obtained about this time from the investigation of the physical properties of aqueous solutions, all pointed in one direction, viz., that the properties of such solutions are the sums of two values, one depending on the metallic constituent of the salt, the other on the non-metallic constituent. The simplest explanation of this fact would be that in such solutions a salt is broken down into two constituents, the one metallic, the other non-metallic, and that each of these constituents has its own distinctive and characteristic properties which are not affected by the presence of the other. This is the simplest and most obvious interpretation of the facts. We shall see later whether it is true.

Berthelot. — It was about 1860 that two men, independently, took up the study of the amounts of heat that are liberated in chemical reactions. The object of this work was not simply to make thermochemical measurements. Far from it. It was recognized that the cause of all chemical reaction is to be found in the thermal change that always takes place whenever substances react chemically, and which was referred to up to that time as the thermal change that "accompanies chemical reactions."

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[1] *Wied. Ann.*, **6**, 168 (1879).

A moment's thought will show that this was confusing cause and effect. It was the energy change that brought about the material change. The study of the former was, then, far more fundamental than the study of the latter, and absolutely essential, if we would ever transform chemistry from pure empiricism into science.[1] This was recognized by Thomsen in Copenhagen, and especially by Berthelot in Paris.

The thermochemical investigations of Berthelot were published in two large volumes[2] in 1879. This work can be referred to here only in so far as it deals with the nature of solution. "These[3] inequalities between the specific heats of solutions of salts, and those of their components, water and anhydrous salt, appear to be due," according to Berthelot, "to the formation right in the solution of certain definite hydrates, comparable with the saline, crystallized hydrates. There is, however, this difference, that the dissolved hydrates exist most frequently in the liquid in a state of partial dissociation, the amount of the dissociation varying with the quantity of the water, and with the temperature.

"The[4] phenomena presented by a normal solution are, in a certain sense, intermediate between those of the simple mixture and the true compound. Indeed, the tendency to unite and form a homogeneous system indicates a real affinity between the solid and the solvent. On the other hand, this union ceases under the influence of simple evaporation, and it takes place apparently in proportions which vary continuously with the temperature." . . . "It[5] appears to me probable, however, that the distinctive feature of solution, in the true sense of the term, lies in the formation of certain definite compounds between the solvent and the dissolved substance. These are the definite hydrates that are formed right in the solution itself, between the salt and the water that is present in the solution, hydrates analogous to, or identical with, those definite hydrates of the same compounds known in the crystalline condition.

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[1] See: *A New Era in Chemistry*, by the Author (D. Van Nostrand Co, N. Y.).

[2] *Essai de Mécanique Chimique, fondée sur la Thermochemie* (1879).

[3] *Essai de Mécanique Chimique*, vol. I, p. 507.

[4] *Ibid.*, vol. II, p. 160.

[5] *Ibid.*, p. 161.

"Let us insist on this point which is very important in chemical statics.

"The[1] chemical statics of solutions depends on the actual state of these different compounds, hydrates or anhydrous substances, actually existing in the solutions. It is therefore extremely important to be able to define this state."

We find also on page 163 the following: "Whatever be the hypothesis relative to the state of the dissolved substances, the actual existence in solution of certain definite hydrates formed by acids, alkalies, and salts is independent of it. It can be established by many demonstrations, on the one hand from the physical properties, on the other from the chemical properties of solutions."

Berthelot then gives a number of these demonstrations, but it would lead us too far to take them up here. What has already been stated will suffice to make clear the views of Berthelot on the nature of solution.

Thomsen. — The other prominent thermochemist was the Dane, Julius Thomsen. He published the results of his thermochemical investigations in his four-volume work, "Thermochemische Untersuchungen." His ideas on solutions are interesting mainly in connection with the relations between solutions and gases. The closing paragraph[2] of the first volume of his great work runs thus: "These investigations lead to the conclusion, that many apparent irregularities in the heat tone, which have been observed when the substances resulting from the reaction of acids and bases are not all soluble, would disappear if all the substances both before and after the reaction were present as aqueous solutions; and that aqueous solutions of substances contain them in a condition, in which, as in the gaseous state, the physical properties are the simplest possible, and can be compared directly with one another."

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[1] *Essai de Mécanique Chimique*, Vol. I, p. 163.

[2] *Thermochemische Untersuchungen*, vol. I, p. 449 (1882).

Thomsen was the *second investigator to recognize the relation between solutions and gases.* Gay-Lussac, it will be recalled, was the first. The importance and significance of the relation will be seen later.

Raoult. — An interesting figure in chemistry at the time that we are now considering was the Frenchman, F. M. Raoult. He carried out his investigations at the University of Grenoble. His work on the lowering of the freezing-point and the lowering of the vapor-tension of solvents by dissolved substances has become a classic.

From his paper[1] published in 1885 the following paragraphs are translated. "The[2] preceding relations show that in all the salts which it enters, every radical plays nearly the same rôle and has the same constitution; and that it always produces the same lowering of the freezing-point, which is nearly independent of the number and the nature of the other radicals with which it can combine." Again, "The[3] molecular lowering of the freezing-point, produced by salts formed by strong monobasic and dibasic acids, is approximately the sum of the partial molecular lowerings of their electropositive and electronegative radicals."

And near the end of his paper, "The[4] diminution in capillary height, the increase in density, the contraction of protoplasm (de Vries' work on osmotic pressure), the lowering of the freezing-point, in brief, most of the physical effects produced by salts on solvent water are the sum of the effects produced separately by the electropositive and electronegative radicals which are contained in them, and which act as if they were simply mixtures in the liquid."

[1] *Ann. Chim. Phys.* [6], **4**, 401 (1885).

[2] *Ibid.*, 414.

[3] *Ibid.*, 417.

[4] *Ibid.*, 427.

"This[1] shows that salts in solution in water ought to be regarded as systems of particles, every one of which is formed of solitary atoms, and, notwithstanding its condition of combination with the others, largely preserves its own individuality, its action, and its characteristic properties.

"The[2] special constitution which we are compelled to recognize for true salts dissolved in water, does not hold for other substances, nor to any appreciable extent in solvents other than water.". . . "The[3] metallic salts themselves, in solvents other than water, show nothing peculiar, and produce the same molecular lowering as all other substances."

Raoult concludes his paper[4] thus: "From this we must conclude that the subdivision of the saline molecules into electropositive and electronegative radicals takes place in fact only in aqueous solutions; and consequently, this is the result of a peculiar chemical act exerted by water on salts dissolved in it."

We are thus coming nearer and nearer to the theory of electrolytic dissociation. Valson concluded that the particles in salts must be regarded as separated from one another. Raoult goes one step farther, and concludes that these particles must be regarded the one as electropositive and the other as electronegative.

Mendeléeff. — We have seen that a large number had held the view that in solution there is some kind of combination between the solvent and the dissolved substance. Most of the ideas that had been expressed were vague and indefinite; indeed they were so general that it was difficult to test them. The views of the great Russian chemist, Mendeléeff, while somewhat indefinite, are far more concrete than those of his predecessors; and the earlier so-called hydrate theory of solution bears his name. His views are expressed in various places in his "Principles of Chemistry."

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[1] *Ann. Chim. Phys.* [6], **4**, 428 (1885).

[2] *Ibid.*, 428. [3] *Ibid.*, 429. [4] *Ibid.*, 430.

Reactions in aqueous solution depend both qualitatively and quantitatively on the mass of the water present, in a word, on the dilution of the solution. Many substances form with water a number of compounds, *e.g.*, many substances crystallize with different amounts of water, and each one of these substances has its own definite and characteristic properties.

He regarded solutions as unstable, but definite, chemical compounds which were undergoing dissociation. The number of hydrates formed by any one substance with water was small. In a great majority of cases there is *only one hydrate* of the substance in question.

Mendeléeff regarded compounds of definite composition as only a special case of compounds of indefinite composition. The indefinite hydrates in solution may be regarded as conforming to the law of multiple proportions, if we consider these hydrates in solution as in a state of dissociation.

To illustrate and fix more definitely in mind the views of Mendeléeff concerning hydrates, let us look more closely into his work on the hydrates formed by sulphuric acid.[1] By plotting the specific gravities of solutions of sulphuric acid of varying concentrations against the concentrations, curves were obtained with maxima in them. These maxima Mendeléeff interpreted as corresponding to the following definite hydrates — H_2SO_4, $H_2SO_4.H_2O$, $H_2SO_4.2H_2O$, $H_2SO_4.25H_2O$, $H_2SO_4.100H_2O$.

Mendeléeff points out that the first two of these compounds are known in the free state, the last three are not thus known. This may be due to a lack of methods for isolating them, or they may not be capable of existing in the free condition.

In a similar manner Mendeléeff concluded that calcium chloride forms the hydrates, $CaCl_2.2H_2O$, $CaCl_2.4H_2O$, and $CaCl_2.6H_2O$. These examples suffice to make clear the idea which Mendeléeff had in mind; certain compounds, especially those that are very hydroscopic or have great power to combine with water, combine with it when in aqueous solution, and form a few definite hydrates. The above examples will show the composition of the hydrates formed by a typical hygroscopic acid and salt.

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[1] *Ber. d. chem. Gesell.*, **1**, 379 (1886).

Mendeléeff furnished very little experimental evidence for the existence of hydrates in aqueous solution, indeed, almost none, and saw no method for determining, even approximately, the composition of the hydrates.

His so-called hydrate theory was, therefore, never more than a qualitative suggestion, and furthermore, has been shown to be erroneous, at least in the case of sulphuric acid.

Testing Mendeléeff's Hypothesis. — In the summer of 1893, the writer was attracted to Stockholm by the fame of that genial investigator — Svante Arrhenius. He suggested that we take up an investigation which, it seemed, would test the hydrate theory of Mendeléeff, as far, at least, as one compound was concerned. We have already seen how Mendeléeff arrived at the conclusion that sulphuric acid in the presence of water yields a few definite compounds with this solvent. This was the conclusion which we decided to test, and in the following way.[1]

Using acetic acid as the solvent, we dissolved in it known amounts of sulphuric acid, and determined how much the freezing-point of acetic acid was lowered by the sulphuric acid. We plotted the curve between the variables, — amount of sulphuric acid and lowering of the freezing-point of a definite amount of acetic acid.

Similarly, we determined the lowering of the freezing-point of a new portion of acetic acid by varying amounts of water, and plotted the curve between the lowering of the freezing-point and the amount of water present.

We then determined the lowering of the freezing-point of acetic acid produced by a known amount of sulphuric acid and a known amount of water, simultaneously. If there is no combination between the water and the sulphuric acid, the lowering in the last case should be the sum of the lowerings in the first two cases. If there is combination, the lowering produced by the sulphuric acid and water simultaneously would be less than the sum of the lowerings produced by them individually.

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[1] *Zeit. phys. Chem.*, **13**, 419 (1894); *Amer. Chem. Journ.*, **16**, 1 (1894).

The latter was found to be the case. When sulphuric acid and water were brought simultaneously into the presence of the acetic acid, the freezing-point lowering was less than the sum of the lowerings when they were added independently. This showed that there was some combination between the sulphuric acid and the water.

By comparing the three sets of lowerings quantitatively, it is a very simple matter to calculate the amount of water in combination with the sulphuric acid. Knowing the total amount of sulphuric acid present and the total amount of water, it is easy to calculate the number of molecules of water in combination with one molecule of sulphuric acid.

We found that sulphuric acid combines with water forming the hydrates — $H_2SO_4.H_2O$ and $H_2SO_4.2H_2O$. When as much as *thirty-seven* equivalents of water were present to one of sulphuric acid, there was no evidence of the formation of hydrates with more water than $H_2SO_4.2H_2O$, *i.e.*, H_6SO_6. The higher hydrates which Mendeléeff thought to be probable, were not found to be present under the conditions under which we worked. If they are capable of existence, it would seem that some indication of them should have manifested itself in this work.

Mendeléeff,[1] from the specific gravity of solutions of alcohol in water, concluded that alcohol is capable of forming the hydrates, $3C_2H_6O.H_2O$, $C_2H_6O.3H_2O$, and $C_2H_6O.12H_2O$. This was tested just as the sulphuric acid had been. Acetic acid was used as the solvent, and the lowering of its freezing-point by water and by alcohol separately and when together, determined. By comparing the three sets of results we may decide whether the water and the alcohol were in a state of combination, and if so, the composition of the hydrates formed.

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[1] *Zeit. phys. Chem.*, **1**, 284 (1887).

The results were unambiguous, and showed that there is not the slightest evidence of any hydrate of alcohol being formed under the conditions of this experiment.

The results of this work as a whole are all against the correctness of the Mendeléeff theory of hydrates. Indeed, the evidence which has been obtained in this laboratory during the past fifteen years, some of which is discussed in the closing chapters of this book, is so decidedly against it as a quantitative expression of the facts, that it can no longer be regarded as tenable.

End of the Qualitative Period. — This ends what may be called the qualitative period in the study of solutions. Several investigators had supposed that there is combination between the solvent water and the dissolved substance, but no one had found any method of determining the composition of the hydrates formed. None of them had even furnished any very conclusive evidence of the existence of these hydrates. No one up to this time had supposed that combination between solvent and solute is a *general phenomenon*, more or less independent, except in magnitude, of the nature of the solvent and of the dissolved substance.

As to the relation between matter in the dissolved and in the gaseous state, what had been pointed out was purely qualitative. As we have seen, Gay-Lussac supposed that there was some analogy between the two states; Horstmann, and Guldberg and Waage made this relation still more probable, and Thomsen laid considerable stress upon it. Mendeléeff saw a relation between the solute in very dilute solutions and matter in the gaseous state; but it remained for another, Van't Hoff, as we shall see, to deduce this relation mathematically and thus place it upon a quantitative basis.

The English chemist, Williamson, and the German physicist, Clausius, supposed that in solutions, acids, bases, and salts, at least, were more or less broken down into their part molecules. Valson was able to explain the additive properties of dilute solutions of salts only on the same assumption; and Raoult, especially from his investigations of the lowering of the freezing-point and of the vapor-tension of the solvent by the dissolved substance, was forced to conclude that the additive property of the constituents of the dissolved substances could be explained only on the assumption that these constituents were practically free from one another in the solution. This again was purely qualitative. It remained for the Swedish physicist, Arrhenius, to prove the correctness of this conclusion, and to furnish quantitative methods for measuring the magnitude of this dissociation. However, before turning to these quantitative generalizations, we must study a property of solutions upon which these epoch-making generalizations rest, *viz.*, their osmotic pressure.

CHAPTER III

THE OSMOTIC PRESSURE OF SOLUTIONS

Traube's Method of Measuring Osmotic Pressure.— It is not a difficult matter to demonstrate the existence in solution of what is known as osmotic pressure. It is only necessary to close the end of a glass tube with parchment paper, put a solution of cane sugar in the tube, and plunge the whole into pure water. The solution cannot pass out through the membrane. Water will pass in and will rise in the tube producing hydrostatic pressure. While it is such a simple matter to demonstrate the existence of osmotic pressure, it is a very difficult matter, indeed, to measure it. Were we dependent on natural membranes for measuring osmotic pressure we would know far less about it at present than we do. Fortunately this is not the case.

In 1867 Mauritz Traube prepared artificial membranes, which have the same osmotic properties as the natural membranes referred to above. When a substance like copper ferrocyanide, formed by the action of potassium ferrocyanide on a solution of a copper salt, is deposited upon a resistant support, it manifests the property of semipermeability, as we say, *i.e.*, allows water to pass through, but does not allow the dissolved substance to pass. The resistant support that is generally employed is an unglazed porcelain cup, the gelatinous precipitate being deposited right in the wall of the cup, or on its surface.

Pfeffer's Preparation of Semipermeable Membranes.— Utilizing the discovery of M. Traube, Pfeffer was able to prepare artificial semipermeable membranes which would not only withstand considerable pressures, amounting to several atmospheres, but which could be used to measure these pressures with a fair degree of approximation.

The work of Pfeffer,[1] published in 1877, contains the first quantitative measurements of osmotic pressure, worthy of the name, that had ever been made. Although more recent work shows that the results of Pfeffer contain very considerable errors, amounting to as much as several per-cent, yet, when we consider that they were the pioneer results in this field, the investigation which led to them must be regarded as of very great value. And, further, when we see to what the results of Pfeffer led, we are almost inclined to regard this as one of the classical investigations of the period in which it was carried out.

A brief discussion of the method employed by Pfeffer for making semipermeable membranes can give no idea of the difficulties which he encountered and overcame. It required several years before he could get even one porcelain factory in Germany to prepare the unglazed porcelain cups sufficiently fine-grained and homogeneous for his purpose. After suitable cups had been obtained, the preparation of membranes which would withstand the pressure without leaking required years of trial. The only way in which to obtain any adequate idea of what Pfeffer did, and what he finally succeeded in accomplishing, is to consult his monograph, referred to above.

Pfeffer's Measurements. — After a suitable membrane had been laid down in the cup, the "cell," as it was called, was then ready for use in measuring osmotic pressure. The solution whose osmotic pressure was to be measured was placed in the cup, which was then closed with a stopper having a manometer attached. The cup was then placed in pure water, and after equilibrium had been established the pressure read on the manometer.

Pfeffer used several gelatinous precipitates as semipermeable membranes. Thus, he deposited in the walls of the cups Berlin blue, calcium phosphate, etc., but found that these substances would not withstand the pressure as well as copper ferrocyanide. Indeed, they would break before the maximum pressure was reached. All of Pfeffer's best measurements were therefore made with copper ferrocyanide as the semipermeable membrane.

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[1] *Osmotische Untersuchungen*, Leipzig, 1877.

Pfeffer's Results.— Pfeffer determined the osmotic pressures of five solutions of *cane sugar*. His results are given in the following table taken from "Osmotische Untersuchungen," p. 81.

Concentrations in percent by weight	Osmotic pressures in centimeters of mercury
1	53.5 cm.
2	101.6 "
2.74	151.8 "
4	208.2 "
6	307.5 "

Gum arabic gave much smaller osmotic pressures.

Concentrations in percent by weight	Osmotic pressures in centimeters of mercury
1	7.1 cm.
6	27.5 "
18	120.0 "

Pfeffer also measured the osmotic pressures of a few solutions of one electrolyte—potassium nitrate. He started with solutions having the concentrations, 1, 2, and 4 weight percent respectively.

It was impossible for him to find a membrane through which this substance would not pass to some extent. There was a constant diminution in the strength of the solution, due to the salt dialyzing through the membrane. He determined the concentrations of the solutions just after reading their osmotic pressures, and obtained the following results[1] — the above concentrations having changed to 0.80. 1.43, and 3.3 percent, respectively.

Concentrations in weight percent	Osmotic pressures in centimeters of mercury
0.80	130.4 cm.
0.86	147.5 "
1.43	218.5 "
3.30	436.8 "

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[1] *Osmotische Untersuchungen*, p. 82.

These results were all obtained at one temperature. Pfeffer measured also the osmotic pressures of certain solutions of different substances at several temperatures. These results are important from the standpoint of the nature of solution, as we shall see later. A few of his results are given below.

The osmotic pressures of a one percent solution of cane sugar were measured at several temperatures between 6.8° and 36°, and the following results obtained.[1]

	Temperatures	Osmotic pressures
a	14.2°	51.0 cm.
	32.0°	54.4 "
b	6.8°	50.5 "
	13.7°	52.5 "
	22.0°	54.8 "
c	15.5°	52.0 "
	36.0°	56.7 "

The apparent irregularities are due to the fact that different cells were used in the several measurements. These are marked (a), (b), and (c). Only those results obtained in the same cell are comparable with one another.

The following results were obtained with a 0.6 percent solution of sodium tartrate.

Temperatures	Osmotic pressures
12.4°	91.6 cm.
37.3°	98.3 "

A saturated solution of acid potassium tartrate gave, at two temperatures, the following results:

Temperatures	Osmotic pressures
13.0°	68.3 cm.
29.2°	115.8 "

These are only some of the results obtained by Wilhelm Pfeffer.

Where Pfeffer Left the Subject of Osmotic Pressure.—Pfeffer was a botanist, and took up the problem of osmotic pressure from a botanical standpoint. He wanted to know something of the magnitude of the force which gives us osmotic pressure. Is it a very small force, or is it one of considerable magnitude? His own results answered this question. A one percent solution of cane sugar showed an osmotic pressure of 53 centimeters of mercury — nearly two-thirds of an atmosphere. A one percent solution contains ten grams in a liter. The molecular weight of cane sugar is 342. Ten grams in a liter is, therefore, only one thirty-fourth normal. A normal solution would, from the work of Pfeffer, have an osmotic pressure of about *twenty-two atmospheres,* which is a force of very appreciable order of magnitude.

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[1] *Ibid.*, p. 85.

Osmotic pressure undoubtedly plays a prominent rôle in plant life. How does the water rise from the bottom to the top of a tree? In the case of the large trees in the West, this rise is often as much as three hundred feet; and the amount of water raised to this height and breathed out through the leaves is enormous. While this problem cannot even yet be considered as completely solved, it is quite certain that osmotic pressure has much to do with it.

The last half of Pfeffer's important monograph[1] is devoted to the bearing of osmotic pressure on plant physiology. It would lead us beyond the scope of this work to discuss this part of Pfeffer's work. Having solved the problem which he undertook to study, *viz.,* the order of magnitude of osmotic pressure, Pfeffer left it at this stage. He did, however, point out the relation between the osmotic pressures of solutions and their concentrations. The osmotic pressures divided by the concentrations gave a constant. He did not seem to see anything very significant in this relation. Osmotic pressure is simply another of those properties which is a linear function of, or proportional to, the concentration of the solution. This amounts to saying that two molecules of a dissolved substance exert twice the osmotic pressure of one molecule, which is not at all surprising.

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[1] *Osmotische Untersuchungen,* Leipzig, 1877.

To a man with a different type of mind, as we shall see, this relation meant far more than simple proportionality. To Pfeffer, it did not.

Other Measurements of Osmotic Pressure. — The results obtained by Pfeffer, while of fundamental importance, were only close approximations. Further, membranes prepared by the Pfeffer method, *i.e.*, by allowing the two solutions which, when they came together, would form the gelatinous precipitate, to soak or diffuse into the walls of the cell, the one from the inside the other from the the outside, were not capable of withstanding very great pressures. The most concentrated solution of cane sugar whose osmotic pressure Pfeffer was able to measure, was a six percent. solution. This was only between one-fifth and one-sixth normal, and had an osmotic pressure of only about four atmospheres.

These results were, therefore, not satisfactory. They were not sufficiently accurate for dilute solutions, and gave no direct clue to the osmotic pressures of even moderately concentrated solutions. Both of these problems have now been solved. We have far more accurate measurements of the osmotic pressures of dilute solutions, and approximate measurements of the osmotic pressures of concentrated solutions. We shall now consider briefly this more recent work.

Work of Berkeley and Hartley on the Osmotic Pressures of Concentrated Solutions. — The Earl of Berkeley and Hartley[1] have devised a method for measuring roughly the osmotic pressures of solutions up to *one hundred and thirty atmospheres*. Their method does not measure directly the osmotic pressure of the solution, but consists in bringing to bear on the solution a pressure which is just equal and opposite to its osmotic pressure, and then measuring the magnitude of this pressure.

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[1] *Trans. Roy. Soc.*, A., **206**, 481 (1906).

The semipermeable membrane of copper ferrocyanide is deposited on the walls of an unglazed porcelain tube. The porcelain tube is surrounded by a tube of gun metal to which a pressure apparatus is attached. Water is introduced into the porcelain tube containing on its walls the gelatinous precipitate serving as a semipermeable membrane. The solution whose osmotic pressure is to be measured is introduced into the gun-metal tube, and therefore comes in contact with the porcelain tube and the semipermeable membrane on the outside.

Water would pass from the porcelain tube through the semipermeable membrane into the solution, but a counter-pressure is brought to bear mechanically upon the solution, and this is increased in magnitude until water appears to cease to flow through the walls of the porcelain tube into the solution. This is determined by having a capillary glass tube attached to the inner side of the porcelain tube and observing whether the height of the water in this tube just remains stationary. If the level of the water in the capillary falls, it means that water is passing through the membrane into the solution, and more mechanical pressure must be brought to bear on the solution to prevent the water from entering. If the water rises in the capillary, it means that water is passing through the membrane from the solution, showing that the mechanical pressure on the solution is greater than its osmotic pressure. The pressure on the solution must be so adjusted that the level of the water in the capillary neither rises nor falls. The mechanical pressure is then just equal to the osmotic pressure of the solution. It is then only necessary to measure the pressure brought to bear on the solution, and we know its osmotic pressure.

Results Obtained. — A few of their results are given below — cane sugar: (molecular weight 342). The concentrations are given in grams per liter. The temperature was 0°.

Grams cane sugar in a liter of solution	Osmotic pressures in atmospheres
180.1	13.95
300.2	26.77
420.3	43.97
540.4	67.51
660.5	100.78
750.6	133.74

The following results were obtained with dextrose.[1]

Grams dextrose in a liter of solution	Osmotic pressures in atmospheres
99.8	13.21
199.5	29.17
319.2	53.19
448.6	87.87
548.6	121.18

The results with mannite are:

Grams mannite in a liter of solution	Osmotic pressures in atmospheres
100	13.1
110	14.6
125	16.7

Five hundred grams of galactose in a liter gave an osmotic pressure of 95.8 atmospheres.

These results must be regarded as only approximations, the necessary error involved being large. They are, however, of the right order of magnitude and are doubtless very nearly the osmotic pressures of these concentrated solutions. We are impressed by their large magnitude. Take the most concentrated solution of cane sugar, which contains 750.6 grams per liter. The molecular weight of cane sugar being 342, this solution is about 2.2 normal. — The osmotic pressure of a normal solution of cane sugar is, as we shall see, between twenty-five and thirty atmospheres, depending on the temperature. The osmotic pressure of a two normal solution of cane sugar is therefore more than three times that of a normal. The meaning of this rapid increase in the osmotic pressure with concentration will become apparent when we come to consider the solvate theory of solution.

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[1] *Trans. Roy. Soc.*, A., **206**, 503 (1906).

Pfeffer's Membranes Would Not Withstand Great Pressures. — Pfeffer, as will be remembered, filled the cells with a solution of potassium ferrocyanide, and then plunged them into a solution of copper sulphate. The two solutions diffused into the walls of the cup, the one from the inside, the other from the outside. Where the copper from the copper sulphate came in contact with the ferrocyanogen group from the ferrocyanide, a precipitate of copper ferrocyanide was formed. By allowing the solution to stand in the cup for the proper length of time before plunging the cup into the copper sulphate, the precipitate would be formed on the inner surface of the cup or anywhere in its wall.

Pfeffer, as will be seen, had to rely entirely upon diffusion to form his membranes, and, as would be expected, the membranes would be only fairly resistant to pressure. They would not withstand great pressure; indeed, only pressures of a few atmospheres.

Electrical Method of Preparing Semi-permeable Membranes. — A method of making semipermeable membranes was discovered in this laboratory, by H. N. Morse, which gives results far more satisfactory than that employed by Pfeffer. Instead of allowing the membrane formers to soak into the walls of the cell, they are driven in electrically. The cell is filled with a solution of potassium ferrocyanide, and plunged into a solution of copper sulphate. One electrode is placed in the cell, and the other around the cell in the solution of copper sulphate. The current is passed from the solution of copper sulphate to that of potassium ferrocyanide. The copper ion, moving with the current, passes into the walls of the cell from the outside; the ferrocyanogen group, moving against the current, passes into the walls of the cell from the inside. Where the two meet they form copper ferrocyanide.

The advantage of this method over the method of Pfeffer is, that by driving the membrane formers into the walls electrically, a much more resistant membrane can be produced than by simply allowing them to soak into the walls. The current is passed until the membrane becomes so compact that the resistance may rise to one million ohms. Membranes formed by this method have been used to measure osmotic pressures of thirty and recently as great as two hundred and fifty atmospheres, with a high degree of accuracy.

It was the discovery of this method of preparing the membranes that led Morse to undertake anew the measurement of osmotic pressure; the result being that he and his co-workers have made measurements of osmotic pressure incomparably the best.

Measurements of Osmotic Pressure Made by Morse, Frazer, Holland and Co-workers. — Provided with the above described method of making semipermeable membranes, Morse and his co-workers began about fifteen years ago a series of measurements of the osmotic pressures of solutions, which, for the difficulties encountered and overcome, and for the accuracy of the results obtained, have become a classic.

For details in connection with this work reference must be had to the original publications.[1] They have measured thus far the osmotic pressures of solutions of cane sugar varying in concentration from one-tenth to normal, and at the following temperatures, — 0°, 5°, 10°, 15°, 20°, 25°, 30°, 40°, 50°, 60°, 70°, and 80°. The solutions were all prepared on a weight normal basis, *i.e.*, so many grams of sugar in one thousand grams of solvent.

The mean osmotic pressures of solutions of cane sugar from one-tenth to normal, and from 0° to 80°, are recorded in the following table.

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[1] *Amer. Chem. Journ.*; during the past fifteen years. *Carnegie Institution of Washington*, Publication No. **198**.

RESULTS WITH CANE SUGAR

OSMOTIC PRESSURES IN ATMOSPHERES
FOR WEIGHT-NORMAL CONCENTRATIONS

TEMP.	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0°	(2.462)	4.723	7.085	9.443	11.895	14.381	16.886	19.476	22.118	24.826
5°	2.452	4.819	7.198	9.608	12.100	14.605	17.206	19.822	22.477	25.280
10°	2.498	4.893	7.335	9.790	12.297	14.855	17.503	20.161	22.884	25.693
15°	2.540	4.985	7.476	9.949	12.549	15.144	17.815	20.535	23.305	26.189
20° ✓	2.590	5.064	7.605	10.137	12.748	15.388	18.128	20.905	23.717	26.638
25°	2.634	5.148	7.729	10.296	12.943	15.625	18.435	21.254	24.126	27.053
30°	2.474	5.044	7.647	10.295	12.978	15.713	18.499	21.375	24.226	27.223
40°	2.560	5.163	7.834	10.599	13.355	16.146	18.932	21.806	24.735	27.701
50°	2.637	5.279	7.974	10.724	13.504	16.314	19.202	22.116	25.123	28.209
60°	2.717	5.438	8.140	10.866	13.666	16.535	19.404	22.327	25.266	28.367
70°	....	...	...	...	13.991	16.820	19.568	22.567	25.562	28.624
80°	....	...	...	....	....	....	....	23.062	25.919	28.818

Ratios Between Gas Pressure and Osmotic Pressure. — As we shall see in the next chapter, the importance of osmotic pressure as bearing on the nature of solution is primarily in connection with the relation between these pressures in solutions and the gas-pressure of gases having the same number of gaseous parts in a given volume that there are dissolved parts in the same volume of the solution. Without going more into detail here on this point, it should be stated that Morse and his co-workers have compared the osmotic pressures of solutions of cane sugar with the gas-pressures of gases; "*the volume of the gas being that of the solvent in the pure state, and not that of the solution.*"[2]

The ratios of osmotic to gas-pressure are given by Morse in the following table:[3]

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[1] These results are taken from *Carnegie Institution of Washington*, Publication No. **198**, pp. 184 and 186 (1914).

[2] *Ibid.*, p. 183.

[3] *Ibid.*, p. 186.

Ratio of Osmotic to Gas-pressure

Temp.	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0°	1.106	1.061	1.061	1.060	1.068	1.076	1.083	1.093	1.104	1.115
5°	1.082	1.063	1.058	1.059	1.067	1.074	1.084	1.093	1.102	1.115
10°	1.082	1.060	1.059	1.060	1.066	1.073	1.083	1.092	1.102	1.113
15°	1.082	1.061	1.061	1.059	1.068	1.073	1.083	1.093	1.102	1.115
20°	1.084	1.062	1.060	1.060	1.067	1.073	1.084	1.093	1.103	1.115
25°	1.084	1.059	1.060	1.059	1.065	1.071	1.083	1.093	1.102	1.113
30°	1.000	1.020	1.031	1.040	1.050	1.060	1.069	1.081	1.089	1.101
40°	1.003	1.011	1.024	1.038	1.046	1.054	1.059	1.067	1.076	1.085
50°	1.000	1.002	1.009	1.017	1.025	1.032	1.041	1.049	1.059	1.071
60°	1.000	1.001	0.999	1.000	1.006	1.014	1.020	1.027	1.033	1.044
70°					1.000	1.002	0.999	1.008	1.015	1.023
80°								1.001	1.000	1.000

"The[1] ratio of osmotic to gas pressure, between 0° and 25°, *is very nearly constant for each concentration of solution.* Omitting the ratio for the 0.1 weight-normal solution at 0°, the mean ratios for the various concentrations are given below."

Concentration weight normal	Mean ratio
0.1	1.083
0.2	1.061
0.3	1.060
0.4	1.060
0.5	1.067
0.6	1.074
0.7	1.083
0.8	1.093
0.9	1.103
1.0	1.114

"The[2] average deviation from these mean ratios is 0.15 percent., while the largest single deviation — that of the 0.6 normal solution at 25°, is 0.3 percent. It is obvious from the relations pointed out above that between 0° and 25° the osmotic pressure of cane-sugar solutions, ranging in concentration from 0.1 to 1.0 weight-normal, obeys the law of Gay-Lussac for gases. In other words, within the limits designated the temperature coefficients of gas and of osmotic pressures are identical."

"The[3] ratios of osmotic to gas pressure between 0° and

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[1] *Ibid.*, p. 183.

[2] *Ibid.*, p. 185.

[3] *Ibid.*, p. 186.

25°, though constant for each concentration, are all greater than unity. The excess varies from 6 per cent in the 0.2, 0.3, and 0.4 normal solutions, on the one side, to 8.3 percent in the 0.1 normal solution; and on the other, to 11.4 percent in the normal solution."

"Having found that the law of Gay-Lussac *does* hold for the osmotic pressures of cane sugar solutions between 0° and 25°, one is inclined to believe that they should also conform to the law of Boyle, and to seek for some rational explanation of the facts: 1st, that the ratios in question are excessive, *i.e.*, above unity; and 2nd, that they are not proportional to the supposed concentration of the solutions. The most obvious general explanation (if one attempts to reconcile the pressures between 0° and 25° to the view that the law of Boyle, as well as that of Gay-Lussac, does hold) is *hydration of the solute*, which may be presumed to have the effect of concentrating the solutions. But if one attempts to work out the precise degree of hydration which would account for the variations of ratio from concentration to concentration, he is quickly entangled in certain hazardous assumptions respecting the relations of solvent to solute and the effect of these upon the osmotic pressure. In the writer's opinion, judgment as to the applicability of Boyle's law to the osmotic pressure of cane-sugar solutions at temperatures below 25° should be suspended until much more is known about the osmotic pressures of the aqueous solutions of other substances."

Summary of Relations. — Morse summarizes these relations as follows:[1] "Between 0° and 25° the ratios of osmotic to gas pressure are all greater than unity, but constant for each concentration. At some temperature between 25° and 30° these ratios begin to decline, but relatively more rapidly in the dilute than in the concentrated solutions. At some temperature (30° for 0.1; 50° for 0.2; 60° for 0.3 and 0.4; 70° for 0.5, 0.6, and 0.7; and 80° for 0.8, 0.9, and 1.0) the ratio becomes *unity* for every concentration."

[1] *Carnegie Institution of Washington*, Publication No. **198**, p. 187.

"The decrease in the ratios of osmotic to gas pressures at temperatures above 25°, suggests an increasing dilution of the solutions through the dissociation of unstable hydrates; and it serves to strengthen the impression that the excessive but constant ratios below 25° are due to the presence of stable hydrates." . . . "It is now important to ascertain whether the ratios, having once declined to unity, maintain that value at all higher temperatures; hence the work of measuring the osmotic pressure of cane sugar at 70° and 80°, and at still higher temperatures, will be resumed as soon as the new cells, previously referred to, have been sufficiently developed for use at those temperatures."

It should be mentioned in connection with this investigation, that a cell containing a 0.5 weight-normal solution was allowed to stand for sixty days after the maximum osmotic pressure had manifested itself, and at the end of this period showed no weakening of the membrane.

Results with Glucose. — Morse and his co-workers measured the osmotic pressures of a series of solutions of glucose of varying concentration. They worked between 0.1 and 1.0 normal, and at 30° and 40° and 50°. It would lead us too far to give the results[1] in detail here. We shall simply quote the conclusions reached.[2] "The foregoing measurements of the osmotic pressures of glucose indicate that, between 30° and 50°, the aqueous solutions of this substance obey the gas laws, since — if we employ the *weight* or *solvent* normal system in making the solutions, and refer the theoretical gas pressure of the solute to the volume of the pure solvent — the ratio of observed osmotic to calculated gas pressure is, in all cases, approximately unity. Stated in another way, the equation of Van't Hoff for very *dilute solutions*, $PV = RT$, applies to *concentrated* solutions of glucose between 30° and 50°, provided we allow the V to signify the volume of the pure solvent instead of the volume of the solution."

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[1] *Ibid.*, p. 196.

[2] *Ibid.*, p. 207.

The meaning of all this will become the more apparent when the relations pointed out in the next chapter are considered.

Results with Mannite. — From the results with mannite the following conclusion was drawn. "It will be seen that all the ratios approach unity, showing that within the limits thus far investigated the aqueous solutions of mannite obey the laws of Gay-Lussac and of Boyle."

Osmotic Pressure of an Electrolyte. — Morse and Frazer have measured the osmotic pressures of a few solutions of one electrolyte — lithium chloride, between the concentrations 0.1 and 0.6 normal; the temperature being 30°.

The enormous difficulties which were encountered in measuring the osmotic pressures of solutions of non-electrolytes, were greatly augmented when the attempt was made to measure the osmotic pressure of any solution of an electrolyte. The reason for this will become clear, when we consider the action of an electrolyte on a colloid like the copper ferrocyanide used for the semipermeable membrane. When we come to study colloidal solutions, we shall see that when an electrolyte (acid, base, and especially salt) is brought in contact with a colloid, the colloid crystallizes and loses its colloidal properties. It was found that when a cell containing a good, semipermeable membrane was filled with a solution of an electrolyte, the membrane rapidly degenerated and soon began to leak. This was probably due to the conversion of the colloidal membrane into the crystalline condition. Sodium and potassium chlorides were so vigorous in their action on the membrane, that the osmotic pressure of even dilute solutions of these substances could not be measured. Lithium chloride in fairly concentrated solution also caused the membrane to degenerate, but in dilute solution its action was so slow that the osmotic pressures of several solutions of lithium chloride were measured with a fair degree of accuracy.

It is a matter of interest to know that membranes which have deteriorated under the action of electrolytes can be restored, in part at least, by standing a long time in contact with pure water. Some two years are required to effect anything like complete restoration. The probable action of the water is to restore the colloidal condition of the membrane; and this raises the question whether water may not have the general tendency to transform crystalloids into colloids. The small number of charged parts contained in it would make this possible, charged parts, as we shall see, tending to convert colloids into crystalloids.

Results with Lithium Chloride. — The following results were obtained for the osmotic pressures of solutions of lithium chloride, ranging in concentration from 0.1 to 0.6 normal, the temperature being 30°.[1]

Concentrations

	0.1	0.2	0.3	0.4	0.5	0.6
Observed pressures	4.325	8.946	13.809	18.755	24.162	29.535
	4.311	9.005	13.626	18.789	....	....
Mean pressures	4.317	8.976	13.768	18.772	24.162	29.535
Calculated gas pressures	2.472	4.943	7.415	9.886	12.358	14.830
Ratio of osmotic to gas pressure	1.746	1.816	1.857	1.899	1.955	1.992

The very large osmotic pressures are due to the substance being an electrolyte, *i.e.*, broken down in solution, as we shall see, into its part molecules, and each part exerting the same pressure as a whole molecule.

That the ratio of osmotic to gas pressure increases with the concentration of the solution, is due to the fact that lithium chloride is one of those substances which in solution combines with a large amount of water, as was shown in this laboratory a number of years ago.[2] The more concentrated the solution, the larger the total amount of water combined with the dissolved substance, and consequently the smaller the percentage of the total water present acting as solvent. The solution is, therefore, much more concentrated than we would suppose, and has a greater osmotic pressure and therefore a higher ratio between osmotic pressure and gas pressure.

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[1] Taken from *Carnegie Institution of Washington*, Publication No. **198**, p. 217 (1914).

[2] *Carnegie Institution of Washington*, Publication No. **60**, p. 31 (1907).

Durability of the Morse Cells. — The discussion of this work by Morse and his co-operators cannot be concluded better than by quoting the following paragraph, which gives an idea of the durability of the cells which they used.

"Particular[1] attention is called to *experiment 2* with the 0.4 weight-normal solution. This is an *endurance* test of the membrane of an unusually thorough character. The cell at the time of setting it up, had a resistance of 1,100,000 ohms and it remained in the bath 145 days. Starting with an initial pressure of 15 atmospheres, it reached an approximate equilibrium in 10 days. The osmotic pressure which the cell sustained during the following 124 days is given in 5 columns, each of 25 daily records. The mean osmotic pressure for the first period was 18,827; for the second 18,894; for the third 18,799; for the fourth 18,636; and for the fifth 18,405. It is believed that a mean of the records for the first 100 days fairly represents the osmotic pressure of the solution. But during the fifth period, *i.e.*, from the 101st to the 125th day of the record, there was a decline in pressure from 18,609 to 18,140 atmospheres, which can only signify that the membrane had at last begun to weaken."

Greater durability than this in a semipermeable membrane could neither be expected nor desired.

A Cell for the Measurement of High Osmotic Pressure. — Frazer, with the co-operation of Myrick, has devised a cell for measuring the high osmotic pressures shown by concentrated solutions. This would allow the laws of Boyle and Gay-Lussac for osmotic pressure to be tested over a wide range of concentration. A cell has been constructed to withstand satisfactorily pressures as high as 250 atmospheres. The position of the membrane is changed in the cell earlier described from near the interior surface of the cell to near the exterior. This same principle has already been successfully used by Berkeley and Hartley, and is necessary in order to have greater strength in the cell wall. It also increases the membrane surface, which insures more rapid adjustment of the equilibrium, diminishing the time for making the measurements. In constructing this apparatus the joints between the metal shell surrounding the cell are made by stiff rubber packing, in such a way that the osmotic pressure tends to tighten the connections. An account of the construction of this cell will soon be published.

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[1] *Carnegie Institution of Washington*, Publication No. **198**, p. 218.

De Vries Method of Measuring the Relative Osmotic Pressures of Solutions. — The methods thus far described measure the absolute osmotic pressures of solutions. Before leaving the subject of osmotic pressure, it seems desirable to discuss at least one method which has been described for measuring the relative osmotic pressures exerted by solutions of a large number of substances. Having worked out the relative osmotic pressures of these solutions, and the absolute osmotic pressure of say one of them, we should of course know the absolute osmotic pressures of them all.

The Dutch botanist, De Vries, was the first to develop and apply a method for measuring the relative osmotic pressures of solutions of a number of electrolytes and nonelectrolytes. His paper[1] bore the title, "Osmotic Experiments with Living Membranes."

The method of De Vries consists in preparing solutions of different substances of such concentrations, that they would each have an osmotic pressure just equal to that of a given solution and, therefore, just equal to one another. The solution with which he compared the solutions whose relative osmotic pressures he was studying, was the contents of the cells of certain plants; and here the difficulty arose in finding the proper plants. We can see what this means after examining the method.

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[1] *Zeit. phys. Chem.*, **2**, 415 (1888); **3**, 103 (1889).

A plant cell to be useful for this work must consist of a solution surrounded by a semipermeable membrane, and this, in turn, surrounded by a more resistant wall of cellulose to prevent the membrane from being easily ruptured. When such a cell is placed in a solution, three things may happen, depending on whether the osmotic pressure of the solution is less than, greater than, or just equal to that of the cell content. If the osmotic pressure of the solution is less than that of the contents of the cell, water will flow from the solution through the semipermeable wall into the cell; this is in accord with the general osmotic principle, that water always flows from the region of lesser to that of greater osmotic pressure. The cell being surrounded by a semipermeable membrane cannot lose its contents, and consequently tends to become distended.

If the osmotic pressure of the solution into which the cell is plunged has an osmotic pressure which is greater than that of the cell contents, water will flow from the cell outward into the solution. The cell having lost water, its contents will shrink, and this can readily be observed under the microscope, if the cell fulfills certain conditions. The third and last possibility is where the osmotic pressure of the solution around the cell is the same as that of the cell content. In this case as much water will pass into the cell in a given time as will pass out, and the cell will preserve its normal appearance.

In order to observe this change in the size of the cell *its contents must be colored,* and here a difficulty arose in finding the proper cells. To quote the words of De Vries, bearing on this point, "Not[1] every plant and not every section can be employed. We need cells in which the plasmolysis can be conveniently observed, and a section in which all of the cells begin to show this phenomenon at exactly the same concentration of the external liquid." The only plants which at that time were known to meet these requirements were: *Tradescantia discolor, Curcuma rubricaulis* and *Begonia*

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[1] *Zeit. phys. Chem.,* **2,** 417 (1888).

manicata, and the section to be chosen was the violet to red upper layer of certain parts of certain leaves.

Method of Procedure. — The cells were placed in the solution whose osmotic pressure it was desired to compare with that of the cells. They were observed through the microscope to see whether water passed into or out of the cell. If water passed into the cell, shown by the cell becoming more distended, it meant that the osmotic pressure of the solution was less than that of the cell contents. In this case the solution was made more and more concentrated, until the cells when plunged into it remained in a perfectly normal condition. When this condition was reached, it meant that the osmotic pressure of the solution was just equal to that of the contents of the cell — the two were, as we say, *isosmotic.*

If, on the other hand, the cell contents shrank when the cell was placed in the solution, it meant that the osmotic pressure of the solution was greater than that of the cell content. In this case the solution was diluted step by step until the cell, in its presence, remained in the normal state. When this was realized, it meant that the osmotic pressures of the solution and of the cell content were equal.

These solutions which, individually, were isosmotic with the contents of a given cell or kind of cells, were isosmotic with one another, *i.e.*, they had the same osmotic pressures.

Isotonic Coefficients. — The isosmotic solutions of a large number of different substances were then analyzed, and their concentrations determined. In this way it was learned what concentrations of different substances have the same osmotic pressure as the contents of a given cell, and, consequently, the same osmotic pressure as one another.

De Vries expressed the concentrations of these isosmotic solutions not in terms of gram-molecules per liter of solution, but he took the reciprocals of the concentrations and called them isotonic coefficients. De Vries worked out a large number of such coefficients. A few of his results are given below.[1]

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[1] *Ibid.*, **2**, 425 (1888).

Compound	Empirical formula	Isotonic Coefficient
Glycerol	$C_3H_8O_3$	1.78
Cane sugar	$C_{12}H_{22}O_{11}$	1.81
Malic acid	$C_4H_6O_5$	1.98
Tartaric acid	$C_4H_6O_6$	2.02
Potassium nitrate	KNO_3	3.0
Sodium nitrate	$NaNO_3$	3.0
Potassium chloride	KCl	3.0
Sodium chloride	$NaCl$	3.0
Calcium chloride	$CaCl_2$	4.33
Magnesium chloride	$MgCl_2$	4.33

The substances that are bracketed are closely related chemically, and it will be observed that they have isotonic coefficients of the same order of magnitude.

Limitations of the Method. — It is evident that this method is limited to those substances and classes of substances which do not act chemically upon the very delicate semipermeable membranes which surround the contents of plant cells. This means that the method is limited practically to solutions of some salts and neutral organic compounds, acids and bases being excluded. However, even with this limitation the method has given results of value.

Other Methods of Determining the Relative Osmotic Pressures of Solutions. — Hamburger[1] found that he could use certain cells of certain animals for measuring relative osmotic pressures, almost as well as De Vries had used cells of plants. The red blood corpuscles of the frog and deer were adapted to this purpose. The structure of these corpuscles is, from our present standpoint, a solution of a large number of things, surrounded by a semipermeable membrane or sac.

The principle of the method is the same as that already described with the vegetable cells.

Wladimiroff[2] used certain bacteria in this same connection, determining by their motions whether the solution into which they were plunged was isosmotic with the contents of the bacteria.

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[1] *Zeit. phys. Chem.*, **6**, 319 (1890).

[2] *Ibid.*, **7**, 529 (1891).

These methods gave results comparable with those obtained by the method of De Vries.

We have now studied the methods of measuring the absolute osmotic pressures of solutions, and the methods of measuring their relative osmotic pressures.

We must next ask, why was osmotic pressure taken up in the present connection? What bearing have the measurements of osmotic pressure on the nature of solution?

We shall see that the work of Pfeffer was fundamental to the recent advances which have been made in our knowledge of matter in the dissolved state. This will be developed in the chapter which follows.

CHAPTER IV

RELATIONS BETWEEN SOLUTIONS AND GASES DEMONSTRATED BY VAN'T HOFF

In the historical development of the present views as to the nature of solution, we saw that Gay-Lussac, as early as 1839, pointed out certain relations between matter in the dissolved and in the gaseous state (p. 30). A similar conception seems to have been held a little later (1845) by an Italian, Bizio; and Rosenstiehl, in 1870, expressed the opinion that there is an analogy between the osmotic force which exists in solutions and the elastic force in gases. Horstmann, in 1869, found that the equations for equilibrium in gases hold for solutions.

We have already become familiar with the views of Guldberg and Waage (p. 36), Thomsen (p. 42) and Mendeléeff (p. 44), on the analogy between solutions and gases.

The great step, however, still remained to be taken,—the mathematical deduction of the relation between matter in these two apparently widely different states of aggregation. This was done by the Dutch chemist, Van't Hoff.

Van't Hoff published, in 1887, an epoch-making paper[1] in the first volume of the "Zeitschrift für physikalische Chemie" on "The Rôle of Osmotic Pressure in the Analogy Between Solutions and Gases." This title will indicate why so much stress was laid in the last chapter on the methods employed for measuring osmotic pressure, and especially upon the results that have been obtained.

Starting with Pfeffer's results, Van't Hoff pointed out the following analogies, and deduced the following relations.

Said Van't Hoff, if there is any fundamental relation between matter in the dissolved and in the gaseous states, then the generalizations or laws which hold for the one condition ought to apply to the other. The best known and most important laws of gas pressure are those of Boyle, Gay-Lussac, and Avogadro.

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[1] *Zeit. phys. Chem.*, **1**, 481 (1887).

The law of Boyle says that the pressure of a gas is proportional to its concentration.

The law of Gay-Lussac states that, volume remaining constant, the pressure of a gas increases $\frac{1}{273}$ for every rise in temperature of one degree centigrade; or, pressure remaining constant, the volume of a gas increases $\frac{1}{273}$ for every rise in temperature of one degree.

The law of Avogadro, as usually stated, is that temperature and pressure being constant, equal volumes of all gases contain the same number of ultimate parts or molecules. For our present purpose it may best be stated as follows: Temperature being constant, equal volumes of all gases which contain the same numbers of independent particles exert the same pressures.

Law of Boyle Applies to the Osmotic Pressures of Dilute Solutions. — From the osmotic pressure results, especially of Pfeffer, Van't Hoff showed that the law of Boyle for gases applies to the osmotic pressures of solutions. He quoted Pfeffer's results,[1] and in the following manner. If we represent the concentrations of the solutions by C, and the osmotic pressures by P, we have the following:

C	P	$\frac{P}{C}$
1 %	535 mm.	535
2 %	1016 "	508
2.74 %	1518 "	554
4 %	2082 "	521
6 %	3075 "	513

The osmotic pressure divided by the concentration is a constant to within the error of Pfeffer's measurements. This means, of course, that the osmotic pressure is proportional to the concentration, which is simply Boyle's law for gases.

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[1] *Ibid.*, **1**, 484 (1887).

Law of Gay-Lussac Applies to the Osmotic Pressure of Dilute Solutions. — Van't Hoff, having found that one of the laws of gas pressure applies to the osmotic pressures of solutions, went farther to see whether other laws of gas pressure apply to solutions. He next tested the applicability of the law of Gay-Lussac.[1] He did this both theoretically and experimentally.

It will be recalled that Pfeffer measured not only the osmotic pressures of a number of solutions of several substances at the same temperature, but also the osmotic pressures of a given solution at more than one temperature. He thus furnished data for calculating the temperature coefficients of osmotic pressure. A solution of cane sugar which at 14.15° exerted an osmotic pressure of 512 mm., at 32° gave a pressure of 544 mm.; while a solution of sodium tartrate, which, at 13.3°, gave a pressure of 1431.6 mm., at 36.6° showed a pressure of 1564 mm.

The temperature coefficients of osmotic pressure, per degree rise in temperature, calculated from the data furnished by Pfeffer, were not $\frac{1}{273}$ as would be expected from the law of Gay-Lussac, but were of this order of magnitude. Were we dependent upon the results of Pfeffer alone to determine the applicability of the law of Gay-Lussac to the osmotic pressures of solutions, we would not be able to say whether the law holds rigidly or not; but fortunately such is not the case.

Here again the work of De Vries and Hamburger comes to our aid. They showed that solutions which were prepared isosmotic at any given temperature remained isosmotic when the temperature was varied. This shows simply that the effect of temperature on the osmotic pressures of the different solutions is the same — the different solutions have the same temperature coefficients of osmotic pressure. This does not show the order of magnitude of the temperature coefficient, and therefore does not show whether the law of Gay-Lussac holds for the osmotic pressures of solutions.

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[1] *Zeit. phys. Chem.*, **1**, 486 (1887).

While we are not able to decide directly the question of the rigid applicability of Gay-Lussac's law to the osmotic pressures of solutions, we can decide it indirectly.

Work of Soret. — In 1881 an interesting and important paper was published by Soret,[1] entitled, "On the State of Equilibrium with Reference to Concentration of a Solid Solution Originally Homogeneous: the Two Parts having been kept at Different Temperatures." This was a continuation of work published by Soret in 1879. The point brought out in this paper is that a homogeneous solution remains homogeneous only as long as the different parts are kept at the same temperature. When one part of an initially homogeneous solution is kept at a different temperature from the other, the solution becomes heterogeneous: the colder part becoming the more concentrated, and the warmer more dilute. This is the "Principle of Soret." The question arises, what causes this difference in concentration? and the answer is obvious, diffusion. The dissolved substance diffuses from the warmer into the colder part of the solution. We shall see later that all diffusion in solution is caused by osmotic pressure, and therefore the principle of Soret enables us to test the applicability of the law of Gay-Lussac to the osmotic pressures of solutions.

If this law holds, then the difference in concentration between the colder and warmer parts of the solution must be $\frac{1}{273}$ of the original concentration for each degree difference in temperature. What was the difference found experimentally?

In his earlier experiments, where the different parts of the solution were allowed to stand at the two temperatures only twenty-three days, Soret found differences in concentration which were always *less* than would be calculated from the law of Gay-Lussac. In his later work,[2] where the tubes containing the solution were allowed to stand, the two parts at the different temperatures, for from fifty to fifty-six days, the differences in the concentrations of the solution in the warmer and in the colder portions were greater than in his earlier experiments, showing that in the earlier work the solution had not stood long enough at the two temperatures to establish equilibrium.

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[1] *Ann. Chim. Phys.* [5], **22**, 293 (1881).

[2] *Loc. cit.*

From Soret's later results Van't Hoff made the following calculations. One part of a solution was cooled to 20° and the other warmed to 80°. The concentration of the cooled portion was 17.33 percent. Assuming Gay-Lussac's law to hold, it was calculated that the concentration of the warmer part of the solution should be 14.3 percent; while the concentration found was 14.03 percent.

In another experiment the concentration in the part of the solution which was at 20° was 29.87 percent. From this it was calculated that the concentration of the part warmed to 80° should be 24.8 percent; while the value found was 23.87 percent.

It will be observed that the concentration calculated for the warmer solution was always slightly greater than that found experimentally, even when the solution had stood, the two parts at the different temperatures, for fifty days.

It has since been calculated that even fifty days is not long enough, under the conditions of Soret's experiments, for the tubes containing the solution to stand in order that equilibrium might be reached. Taking this into account, and the comparatively small difference noted above between the values found and those calculated, we seem reasonably safe in concluding that the law of Gay-Lussac for gases, like the law of Boyle, applies to the osmotic pressure of solutions.

Equality of Gas-Pressure and of Osmotic Pressure.—We have shown that gas-pressure is proportional to osmotic pressure. The applicability of the two laws of gases just considered establishes this relation. What we want to know, however, is the relation between the actual osmotic pressure and the actual gas pressure when the gas and the solution are of the same concentration, *i.e.*, contain the same number of parts in a given volume — does Avogadro's law for gases apply to solution?

Van't Hoff has furnished this information.

The way to test this point is to prepare a solution of known concentration, *i.e.*, containing a certain number of dissolved parts in a certain volume of the solution; and determine the osmotic pressure of this solution. Then take a gas of such concentration that it contains the same number of gas-particles in the same volume. Measure the pressure of this gas. Then compare directly the osmotic pressure of the solution with the gas-pressure of the gas. This comparison was made by Van't Hoff.[1]

He took a one percent solution of cane sugar, *i.e.*, a solution containing one gram of sugar in one hundred grams of water. This solution, considered from the standpoint of volume, contains a gram of sugar in 100.6 c.c. of solution. From Pfeffer's data Van't Hoff calculated the osmotic pressure exerted by such a solution.

If we compare this with the gas-pressure exerted by a quantity of gas, say hydrogen, containing the same number of gas particles as there were sugar particles in the same volume, we would have the following:

Temperature (t)	Osmotic pressure	Gas pressure
6.8°	0.664 mm.	0.665 mm.
13.7	0.691	0.681
14.2	0.671	0.682
15.5	0.684	0.686
22.0	0.721	0.701
32.0	0.716	0.725
36.0	0.746	0.735

The above data show that the two pressures are approximately equal to one another, under the same conditions of concentration and temperature.

A moment's thought will show that this equality is very surprising. Think, on the one hand, of a gas. The particles are free to move, and do move with very high velocities, exerting a pressure due to their impacts against the walls of the containing vessel.

Think, on the other hand, of a solution. The dissolved particles move very slowly through the viscous liquid. The osmotic pressure which they exert, it seems, can never be accounted for on a purely kinetic basis. Indeed, we do not know today what is the cause of osmotic pressure. Yet, osmotic pressure in result, *i.e.*, in order of magnitude, is equal to gas-pressure. This shows, of course, since Avogadro's law holds for the gas-pressures of gases, that it must hold for the osmotic pressures of solutions.

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[1] *Zeit phys. Chem.*, 1, 493 (1887).

Van't Hoff[1] also deduced this same relation on purely theoretical grounds.

Importance of the Applicability of the Gas-Laws to Solutions. — We must now ask what has been gained by showing that the laws of gas-pressure apply to the osmotic pressures of solutions? How does this aid us in dealing with the problem of solutions?

About matter in the solid state we really know very little. We know the shapes of the crystals which it forms. We know a little about the passage of the various forms of energy — light, heat, electricity — through solids; but this knowledge is after all superficial. Our ignorance of the real nature of solids is very nearly perfect.

When we turn to liquids, we know very much more about them than we do about solids. We know the molecular weights of substances in the liquid state; we have studied pretty thoroughly the physical properties of liquids. In a word, we know a good deal about liquids; but even here what we know is comparatively little in comparison with what we do not know.

When we turn to gases, we really know much more. Here is matter in the most dilute and in the simplest state. The laws of gases are comparatively simple, and are pretty well understood. Matter in the gaseous state lends itself to mathematical treatment as matter in no other state of aggregation does, and this is the most important point. We can apply the only rigid and exact scientific method — the mathematical — to gases.

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[1] *Zeit. phys. Chem.*, **1**, 489 (1887).

Van't Hoff in this work, then, has shown that we can deal with solutions largely as we deal with gases — since they both obey the same fundamental laws; and this is a great step forward in our dealing with solutions. We can now deal with them, to a very considerable extent, by the exact mathematical method, and thereby place our knowledge of dissolved substances upon a more scientific basis.

In the first chapter of this work, attention was called to the importance of solution for science in general, and for chemistry in particular. We saw that it is absolutely essential for chemistry — chemistry is a branch of the science of solutions. Now that we can deal with solution by the truly scientific method — the mathematical — and since solution lies right at the foundation of all chemistry, it is obvious that we have made good progress in the direction of converting chemistry into a branch of exact science, like the sister science, physics. Much has already been accomplished in this direction. Chemistry is becoming more and more mathematical, and will become still more mathematical in the near future. This is due in no small degree to the relations pointed out by Van't Hoff between solutions and gases.

The importance of this generalization, mathematically deduced, cannot be easily overestimated. If the author were asked to select the most important generalization which has ever been reached in chemistry, tending to convert chemistry from empiricism into science, he would unhesitatingly name the application of the gas laws to solution.

Although this was hinted at in a qualitative way by several before the time of Van't Hoff, it remained for this great Dutch chemist, at the age of thirty-five, to deduce these relations mathematically, and thus place them once for all upon a scientific basis.

Exceptions to the Above Relations.— Van't Hoff has, then, shown that the three fundamental laws of gas-pressure — the laws of Boyle, Gay-Lussac, and Avogadro — apply to the osmotic pressures of solutions. While this is true, it is not the whole truth. These laws apply to the osmotic pressures of solutions of certain kinds of substances, but they do not apply at all to the osmotic pressures of solutions of other types of compounds.

These laws hold for solutions of nonelectrolytes, *i.e.*, solutions of substances which do not conduct the current. These include all of the neutral organic compounds; in a word, all substances except acids, bases, and salts. The gas laws do *not apply to the osmotic pressure of a single electrolyte;* and the electrolytes, acids, bases, and salts, are by far the most interesting and important chemical compounds. They are the active substances, the things that primarily give us chemistry. The nonelectrolytes are comparatively inactive.

Van't Hoff called attention to the fact that the *electrolytes exert too great osmotic pressure*, in terms of that exerted by the nonelectrolytes, which, we have seen, was exactly equal to that exerted by gases at the same concentration as the solution of the nonelectrolyte.

Even Van't Hoff could not explain this discrepancy presented by the electrolytes. This remained for another — Svante Arrhenius.

CHAPTER V

THE THEORY OF ELECTROLYTIC DISSOCIATION AS ANNOUNCED BY ARRHENIUS

In Chapter II of this work, we saw that a number of investigators had in mind the conception that in solution molecules of substances are in some way broken down into parts.

Williamson (p. 31) was forced to this conclusion from his study of the action of sulphuric acid on alcohol.

Clausius (p. 33), from the study of the electrical behavior of solutions of electrolytes, concluded that such solutions must contain not only whole molecules, but also part molecules.

From the additive property of the constituents of salt solutions Valson (p. 36) thought that the constituents of the salt in solution must be in a state of virtual independence, and Favre and Valson (p. 38) were of the same opinion.

Kohlrausch (p. 40) discovered the law of the independent migration velocities of the ions — another additive property of solutions, and Raoult (p. 43) added other new properties of solutions — lowering of freezing-point and lowering of vapor-tension — to those which were the sum of the corresponding properties of the constituents of the dissolved substances.

The Italian, Bartholi, in 1882, seemed to have had in mind some conception of dissociation of the dissolved parts in solution.

It remained, however, for the young Swedish physicist, Svante Arrhenius, to give us the theory of electrolytic dissociation in the form in which we now have it, and which has proved to be one of the corner stones in the epoch-making developments in chemistry during the last thirty years.

Arrhenius and the Dissociation Theory. — Just at the time (1887) that Van't Hoff encountered the apparent discrepancies presented by electrolytes, in regard to the relations between solutions and gases, this young Swede came to his laboratory. In 1883 Arrhenius had studied the electrical conductivity of solutions of electrolytes, and in 1884 had published the view that such solutions contain two kinds of molecules, those that conduct because they are decomposed into their part molecules, and those that do not conduct because they are present as whole molecules. With this conception in mind, Arrhenius turned to the problem of the meaning of the abnormally large osmotic pressures exerted by electrolytes, which do not obey the laws of gas-pressure, and which compelled Van't Hoff to introduce into the simple gas equation $PV = RT$, the coefficient i, which was always greater than unity, in order that the equation might be applied to the osmotic pressures of such solutions. What is the significance of these abnormally great osmotic pressures?

The problem seems to have presented itself to Arrhenius' mind about as follows. The osmotic pressures of solutions of nonelectrolytes obey the law of Boyle. This simply means that these osmotic pressures are a function of numbers — of the ratio between the number of parts of the dissolved substance and the number of parts of the solvent. This is what might be called an arithmetical property.

Since osmotic pressure is a function of numbers and numbers only, when we have too great osmotic pressure we must have a too great number of parts present. This conclusion is unavoidable. The solution of this problem to a mathematical-physical mind like Arrhenius', was obvious. If we want to account for a larger number of parts than correspond to the whole molecules, we must consider these whole molecules as broken down into such parts, and this is what Arrhenius did.

He assumed that molecules of acids, bases, and salts in solution are broken down, or dissociated, into parts; these parts being shown to be charged because they conduct the current. Arrhenius, however, went much farther than this. He did not simply say, as did Clausius, that *some* of the molecules of an electrolyte are broken down into part molecules, but in his epoch-making paper published in the first volume of the "Zeitschrift für physikalische Chemie,"[1] he points out methods for determining the relative numbers of the molecules that are broken down or dissociated into part molecules.

Arrhenius Points out Methods of Measuring Dissociation.[2] — As has been stated, as early as 1883 Arrhenius was working on the property of aqueous solutions of electrolytes to conduct the current. The part molecules are those which carry the current, and these he termed the "active" molecules. Those molecules which do not take part in conducting the current he termed "inactive." The inactive whole molecules break up into the active part molecules, called *ions*, which are free to move independent of one another. In the inactive molecules the constituents are bound to one another. As we increase the dilution of a solution, the inactive molecules pass over into active, until at great dilution practically all of the molecules have become active. Arrhenius calls the ratio between the number of active, and the sum of the active and inactive molecules the "activity coefficient." When all of the inactive have passed over into active molecules, this coefficient is, of course, unity; for smaller dilutions less than unity. For any dilution the activity coefficient, which is what we today call the percentage dissociation α, is the ratio between the molecular conductivity at the dilution in question (μ_v), and the molecular conductivity infinite dilution (μ_∞).

$$\alpha = \frac{\mu_v}{\mu_\infty}$$

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[1] *Zeit. phys. Chem.*, **1**, 631 (1887).

[2] *Ibid.*, p. 633.

Knowing the activity coefficient, we can calculate the value of i in the Van't Hoff equation for osmotic pressure. If we represent the number of ions into which every molecule breaks down by k,

$$i = 1 + (k - 1)\,a$$

The coefficient i can also be calculated from the lowering of the freezing-point. i is the ratio between the molecular lowering of the freezing-point observed, and the molecular lowering if there were no dissociation. Let us represent the former by t, the latter is 18.5 for water; the coefficient i is calculated thus:

$$i = \frac{t}{18.5}$$

The terms molecular conductivity and molecular lowering of the freezing-point have recently been used. Molecular conductivity means the actual conductivity divided by the concentration expressed decimally, and molecular lowering of the freezing-point means the actual lowering of the freezing-point divided by the concentration expressed decimally.

Dissociation from Freezing-Point Lowering Compared with Dissociation from Conductivity. — Probably the most striking feature of Arrhenius' paper is his comparison of electrolytic dissociation as calculated from freezing-point measurements, with the results obtained from the study of the conductivity of solutions. A few of his results for nonelectrolytes, and for acids, bases, and salts are given below.[1]

NONELECTROLYTES

Compound	Formula	a	$i = \frac{t}{18.5}$	$i = 1 + (k - 1)\,a$
Methyl alcohol	CH_4O	0	0.94	1.00
Glycerol	$C_3H_5(OH)_3$	0	0.92	1.00
Cane sugar	$C_{12}H_{22}O_{11}$	0	1.00	1.00
Acetone	C_3H_6O	0	0.92	1.00
Ethyl acetate	$C_4H_8O_2$	0	0.96	1.00
Acetamide	$C_2H_3ONH_2$	0	0.96	1.00

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[1] *Zeit. phys. Chem.*, **1**, 634 (1887).

Acids

Compound	Formula	a	$i = \frac{t}{18.5}$	$i = 1 + (k - 1)\,a$
Hydrochloric acid	HCl	0.90	1.98	1.90
Nitric acid	HNO_3	0.92	1.94	1.92
Sulphuric acid	H_2SO_4	0.60	2.06	2.19
Hydrogen sulphide	H_2S	0.00	1.04	1.00
Hydrocyanic acid	HCN	0.00	1.05	1.00
Acetic acid	CH_3COOH	0.01	1.01	1.01
Malic acid	$C_4H_6O_5$	0.04	1.08	1.07

Bases

Compound	Formula	a	$i = \frac{t}{18.5}$	$i = 1 + (k - 1)\,a$
Sodium hydroxide	$NaOH$	0.88	1.96	1.88
Potassium hydroxide	KOH	0.93	1.91	1.93
Calcium hydroxide	$Ca(OH)_2$	0.80	2.59	2.59
Strontium hydroxide	$Sr(OH)_2$	0.86	2.61	2.72
Barium hydroxide	$Ba(OH)_2$	0.84	2.69	2.67
Ammonia	NH_3	0.01	1.03	1.01
Methylamine	CH_3NH_2	0.03	1.00	1.03
Ethylamine	$C_2H_5NH_2$	0.04	1.00	1.04

Salts

Compound	Formula	a	$i = \frac{t}{18.5}$	$i = 1 + (k - 1)\,a$
Potassium chloride	KCl	0.86	1.82	1.86
Sodium chloride	$NaCl$	0.82	1.90	1.82
Potassium bromide	KBr	0.92	1.90	1.92
Sodium nitrate	$NaNO_3$	0.82	1.82	1.82
Sodium acetate	CH_3COONa	0.79	1.73	1.79
Potassium chlorate	$KClO_3$	0.83	1.78	1.83
Sodium carbonate	Na_2CO_3	0.61	2.18	2.22
Ammonium sulphate	$(NH_4)_2SO_4$	0.59	2.00	2.17
Barium nitrate	$Ba(NO_3)_2$	0.57	2.19	2.13
Strontium nitrate	$Sr(NO_3)_2$	0.62	2.23	2.23
Lead nitrate	$Pb(NO_3)_2$	0.54	2.02	2.08
Cupric acetate	$(C_2H_3O_2)_2Cu$	0.33	1.68	1.66
Mercuric chloride	$HgCl_2$	0.03	1.11	1.05
Cadmium nitrate	$Cd(NO_3)_2$	0.73	2.32	2.46

The importance of these quantitive results is very great indeed. The agreements are far too close and exist in such a large number of cases, that it is impossible to account for them as due to accident. The impression that these relations made upon the scientific world was very deep. There were agreements that could not be ignored, and although the assumption upon which they were calculated was quite revolutionary in character, it seemed from these agreements that it must contain a large element of truth. These results undoubtedly did more to attract men of science to the Arrhenius' theory than any other one argument bearing upon it.

Arrhenius, in discussing these relations, calls attention to the fact that in making these calculations he has made two assumptions: viz., that the law of Van't Hoff, or the relations between the osmotic pressure of solutions and the gas-pressure of gases, holds not simply for nonelectrolytes, but also for the electrolytes, provided we take into account their degree of dissociation; and, secondly, that an aqueous solution of any electrolyte is partly dissociated, *i.e.*, consists partly of undissociated molecules and partly of ions, the relative numbers of the two being a function of the dilution of the solution. As the dilution of the solution is increased the number of active molecules increases, the dissociation becoming complete at infinite dilution.

Arrhenius then takes up a discussion of certain properties of solutions which are additive, *i.e.*, they are the sum of the corresponding properties of the ions of the solution. With certain of these properties we are not yet supposed to be familiar, and they will therefore not be discussed in this connection.

Bearing of the Theory of Electrolytic Dissociation on Chemistry. — The theory of electrolytic dissociation, as it was given us by Arrhenius, says that dilute solutions of acids, bases, and salts contain practically ions only, and very few molecules. It will be recognized that ions are the substances which are the most active chemically. If dilute solutions of these substances contain only ions and practically no molecules, then the chemical activity of these solutions cannot be due to molecules, since there are but few molecules present, but must be due to the ions. It was further shown that dilute solutions of acids, bases and salts are more active, if we take into account the dilution, *i.e.*, refer everything to molecular quantities, than more concentrated solutions. For example, a thousandth normal solution of an acid is more than one-thousandth as active as a normal solution. This would indicate not only that ions are chemically active, but that they are the most active chemical agents.

This conclusion at the time we are considering was revolutionary. Chemists prior to this time had always looked upon atoms and molecules as the active agents of chemistry. Indeed, atomic and molecular chemistry was well-nigh universally accepted. Chemists had become accustomed to think of reactions in terms of molecules and atoms, and now to ask them to lay all this aside, and start over again, thinking only of ions or charged parts as effecting chemical reactions, was asking a good deal. Indeed, it was soon seen that not only are ions the most active agents chemically, but facts were brought to light which made it highly probable that *ions are the only active chemical agents*. Ions were apparently necessary in order that we might have a chemical reaction. Ions could react with molecules and with other ions, but molecules could not react with other molecules. Some facts bearing on this point have been discussed in the first chapter of this book.

This was going very far indeed. To ask chemists to add to atomic and molecular chemistry, ionic chemistry, would be asking much; but to ask them to abandon atomic and molecular chemistry and to substitute for it ionic chemistry was sure to arouse opposition, especially on the part of those who had been accustomed for a long time to think and work in terms of atoms and molecules.

Opposition to the Theory of Electrolytic Dissociation. — Almost as soon as Arrhenius proposed the dissociation theory a storm, indeed in certain quarters a veritable cyclone, of opposition to the theory broke loose. In some cases this opposition was based on a careful study of the facts, and, in other cases, on an inability or an indisposition to adapt one's self to the new ideas.

A careful examination will show that in some cases the opposition to the theory of electrolytic dissociation was based in no small measure upon a certain lack of familiarity with the subject that was being discussed. For example, it was said that the theory of electrolytic dissociation could not be true, because metallic sodium and metallic potassium could not remain in the presence of water without acting chemically upon it. This, of course, entirely failed to distinguish between an atom and an ion. An atom is uncharged, or electrically neutral; an ion is charged. There is no reason for judging of the properties of a charged atom or group of atoms, from the corresponding properties of the same atom or group when uncharged; and this kind of criticism, therefore, had no scientific significance.

This example is cited to illustrate a certain type of criticism to which the theory of electrolytic dissociation was subjected in its early days. It is obvious that this type was based largely upon a misconception of the meaning and of the significance of the theory of electrolytic dissociation.

There was, on the other hand, a more conservative criticism of the theory, on the part of many who had no case to advocate, no preconception as to the truth in the matter, no strong prejudice to overcome. They were prompted only by the desire to get at the truth; and the new theory was called upon to prove its case. This kind of criticism is always wholesome. It is not obstructively conservative, but the new theory or generalization which would supplant existing views, is called upon to prove itself. This is exactly right, and it is this kind of criticism that gets at the truth. Those critics of the dissociation theory who belonged in this class studied the new theory in as many of its bearings as possible. They looked into the facts underlying the theory to see on what kind of a foundation it rested, and then proceeded to ask questions.

They made one point which was at that time absolutely unanswerable.

Relations Between Solutions and Gases and the Theory of Electrolytic Dissociation Hold Only for Dilute Solutions. — Attention was called to the fact that the relations pointed out by Van't Hoff between solutions and gases, as well as the theory of electrolytic dissociation itself, hold only for dilute, and indeed, only for very dilute solutions. These relations hold rigidly only for what was termed "ideal solutions." Said the critics of the dissociation theory, this may all be very well as far as it goes, but it does not go far enough. We want a theory of solution which does not apply simply to very dilute or "ideal solutions," but which holds for all solutions. It was pointed out that these relations hold only for solutions so dilute that they have little or no significance in chemistry. They do not apply to the ordinary solutions that we use in the chemical, physical, biological, or any other scientific laboratory.

It was insisted, and rightly so, that this is a serious defect in the dissociation theory and in the relations between the osmotic pressures of solutions and the gas pressures of gases. These relations and this theory of solution which was the outcome of these relations bear somewhat the same relation to a comprehensive theory of solution as the laws of Boyle and Gay-Lussac do to a comprehensive law of gas-pressure which would apply under a great variety of conditions, such as the equation of Van der Waals.

This objection was not answered, and in the light of the facts then known could not be. It was a weak point in the relations between solutions and gases demonstrated by Van't Hoff, and in the theory of electrolytic dissociation as proposed by Arrhenius.

It seems that we now have the partial explanation of why it is that these relations and this theory did not appear to hold for the more concentrated solutions. This will be discussed at some length in the last two chapters of this work.

CHAPTER VI

DIFFUSION IN SOLUTION

The Phenomenon of Diffusion. — When a solution of a given concentration is brought in contact with the pure solvent, or with a solution of the same substance at a different concentration, the dissolved substance passes over from the more concentrated to the more dilute solution, and continues to do so until equality of concentration is established.

Place a solid in the bottom of a tall vessel and fill the vessel with a liquid in which it is soluble. The solid will dissolve and pass upward through the solvent to the surface.

The above holds true for the heaviest solids and the lightest solvents. The substance to be dissolved may be heavy, such as a salt of lead or platinum, and the solvent may be water or some much lighter liquid. The above will take place regardless of the relative specific gravities of the two. This is, of course, the well-known phenomenon of diffusion; but we are so familiar with the results of diffusion that we are often not inclined to stop and think of its cause.

A moment's thought will show that this is a very remarkable phenomenon — a heavy salt rising against the pull of gravity through a very much lighter liquid.

Diffusion Caused by Some Force. — To accomplish either of the above results it is obvious that some force is necessary, and the question arises, what is the force that causes diffusion?

If we examine all of the known forces in solution, we will soon come to the conclusion that there is only one which can possibly cause diffusion, and that is osmotic pressure, or the force which causes osmotic pressure. If this is the only known force in solution which can cause diffusion, why not conclude at once that the cause of diffusion is osmotic pressure? The answer is of course obvious. There may be in solution some force at present unknown to us which is the cause of the phenomenon we are considering.

Is osmotic pressure the cause of diffusion? The question can be answered in only one way. Study the phenomena presented by osmotic pressure and discover their laws. Study the phenomena of diffusion and discover their laws, and then see whether the two classes of phenomena obey the same laws. This is exactly what has been done in the cases of diffusion and osmotic pressure. With what result we shall now see.

Work of Graham on Diffusion. — The pioneer in the study of diffusion in a scientific manner was the English chemist, Thomas Graham.[1] Graham's method of studying diffusion was very simple. The solution was poured into a glass vessel, and water poured on top of the solution until the vessel was filled. This vessel containing the solution was then placed in a glass cylinder, which was filled with water until the level of the water in the cylinder was a few centimeters above the top of the vessel containing the solution. The whole system was then set in a quiet place at a constant temperature, and allowed to stand for a certain definite period of time. An analysis of the solution in the outer cylinder gave the amount of the dissolved substance, which, in a given time, under the given conditions, had diffused from the inner vessel into the outer.

Graham found that the mass of the substance that diffuses is largely dependent on the nature of the substance. Acids diffuse much more rapidly than salts. Salts, in turn, diffuse with very different velocities. With mixtures of salts the constituents diffused with velocities which were characteristic of the individual salts; and each diffused practically as if it alone were present.

"If[2] two salts mix without combining with one another, we may expect that both will diffuse separately and independent of one another; each salt obeying its own specific power of diffusion."

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[1] *Phil. Trans.*, **1**, 805 (1850), and 483 (1851). *Lieb. Ann.*, **77**, 56 and 129 (1851); **80**, 197 (1851).

[2] *Lieb. Ann.*, **77**, 75 (1851).

Graham utilized this independent diffusibility of salts from their mixtures to effect separations of such mixtures into their constituents. "From[1] what has been said, it is clear that diffusion furnishes us with a means of separating salts to a certain extent, according to the same principle by which volatile substances of different boiling-points can be separated by distillation."

This applies especially to salts which are decomposed by water, such as acid potassium sulphate, the alums and other double salts. From solutions of these substances the constituents can be separated to a greater or lesser extent by diffusion.

Graham also studied the effect on the diffusion of a salt, of dissolving it in a solution of another salt. He wanted to see whether the diffusion of a salt in a solution of another salt bore any relation to its diffusion in pure water. He could detect no difference under the two sets of conditions.

While Graham showed that the amount of diffusion is approximately proportional to the concentration, he did not arrive at the fundamental law of diffusion. This was left for Fick.

The impression which the work of Graham made upon his contemporaries is shown by the following editorial comment on the first paper published on this subject by Graham.[2]

"The above investigation of Professor Graham calls attention to the existence of a new cause, or a new property of heterogeneous substances, which exerts a definite effect on the affinity in the chemical compound. That the salt content of a salt solution which is covered with pure water, distributes itself gradually from below towards the surface of the water, is a well-known fact, but that different substances have this capability to a very unequal degree, that

[1] *Lieb. Ann.*, **77**, 76 (1851).

[1] *Ibid.*, **77**, 56 (1851).

each obeys its own specific law of diffusion, that in consequence of this inequality the water supernatant to a solution of mixed salts receives the mixed salts in a different proportion from that in which they exist in the lower layers, that under these conditions, alum, in consequence of the unequal diffusibility of its constituents, is decomposed, that due to the same cause a solution of potassium sulphate in lime water is decomposed; all these are such remarkable and unexpected results that they are to be ranked among the most important contributions to science in recent times." This note is signed "The editor"; and the "Annalen" was edited at that time by Friedrich Wöhler, Justus Liebig and Hermann Kopp.

The Generalization of Fick. — Fick studied the diffusion of solutions with special reference to the relation between the amounts of substances that diffuse, the concentrations of the solutions and the differences in concentrations between diffusing solutions. The result is the generalization known as the law of Fick.[1] This law may be formulated as follows:

"The[2] dissemination of a dissolved substance through a solvent, as far as it takes place undisturbed under the influence of molecular forces alone, obeys the same laws which Fourier established for the dissemination of heat in a conductor, and which Ohm announced for the conduction of electricity. In the Fourier law it is only necessary to replace the words *quantity of heat* with the words *quantity of dissolved substance,* and the word *temperature* with *density of solution.*"

In a word, Fick showed that diffusion is proportional to difference in concentration.

Effect of Mass on Diffusion. — From the law of Fick it can be seen at once that the result of diffusion is to make the whole system homogeneous. No matter what the original difference in concentration may have been, no matter what the nature of the substance or substances diffusing, no matter what the nature of the solvent or solvents involved; the dissolved substance diffuses over from the region of greater to that of lesser concentration, and this continues until equality of concentration is established in all parts of the solution. This must be regarded as one of the fundamental facts in connection with solution. If this fact is considered with that to which attention was called earlier in this paper, that diffusion is a phenomenon which seems largely to defy gravitation, we realize the remarkable nature of the property with which we are dealing.

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[1] *Pogg. Ann.*, **94**, 59 (1855).

[2] *Ibid.*, **94**, 65 (1865).

When we think of very heavy salts rising vertically through comparatively light liquids, however, we cannot avoid the question as to whether the mass of the diffusing substance does not have something to do with its diffusibility, if not with the final conditions of equilibrium of the diffusing system.

Beudant,[1] in 1818, announced that he had made the observation that when unsaturated solutions were allowed to stand, crystals separated on the bottoms of vessels containing such solutions. This observation, if correct, would be of the very greatest importance as bearing on the problem in hand.

It attracted the attention of Gay-Lussac,[2] who at once repeated the experiment. He quotes Beudant,[3] "I have remarked that crystals are formed without any evaporation from solutions otherwise very dilute." Beudant states that he took proper precautions to prevent any evaporation of the solutions.

Says Gay-Lussac,[4] "I have taken two glass tubes two meters long and three centimeters in diameter. I placed in one a saturated solution of niter, at the temperature of the vault of the observatory, and in the other a solution of marine salt, also saturated; two other tubes were filled with similar solutions in which there were not more than four centigrams of each salt. These tubes, hermetically sealed, remained six months in the vaults of the observatory in a vertical position. At the end of this time I determined by evaporation the quantity of salt contained in the water of the upper and of the lower part of the tube, and found that the solutions were perfectly homogeneous."

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[1] *Ann. Chim. Phys.* [2], **8**, 15 (1818).

[2] *Ibid.* [2], **11**, 306 (1819).

[3] *Ibid.* [2], **8**, 15 (1818).

[4] *Loc. cit.*

Gay-Lussac then attempts to explain the source of error in Beudant's experiments. It would lead us too far to discuss this here, and it is not necessary, since they are probably wrong.

In a paper by Lieben,[1] "On the Homogeneity of Solutions," he studies the above question for solutions of both solids and gases. He states that his results justify the conclusion that, "So[2] far as our present knowledge goes, in a homogeneous solution which is allowed to rest quietly, a settling of the particles of salt from the upper to the lower layers does *not* take place."

This same question has been discussed thermodynamically by Gouy and Chaperon, and the conclusions tested by experimental results; in a paper on the concentrating of solutions by weight,[3] they show that weight has no effect provided the solution does not change in density when subjected to small changes in concentration. If the density increases with increase in concentration, the lower layers become more concentrated.

From the vapor-tension measurements of Wüllner and Moser[4] the authors calculate the difference in concentration between the uppermost and lowest layers of a solution 100 meters deep.

They obtained the following results:

	At top	At bottom	Difference
Cadmium iodide	0.166	0.153	0.013
Sodium nitrate	0.20	0.196	0.004
Sodium chloride	0.11	0.1095	0.0005
Sugar	0.55	0.546	0.004

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[1] *Lieb. Ann.*, **101,** 77 (1857). [2] *Ibid.*, 83.

[3] *Ann. Chim. Phys.* [6], **12,** 384 (1887).

[4] *Pogg. Ann.*, **103,** *Wied. Ann.*, **3,** (1881).

These differences are obviously very small.

Temperature Coefficients of Diffusion — Principle of Soret. — Diffusion as it takes place ordinarily is a very slow process. It requires months and, under certain conditions, many months to establish equilibrium where diffusion alone establishes the equilibrium. This condition is accelerated by rise in temperature — the higher the temperature, other things being equal, the more rapid the diffusion. What are the temperature coefficients of diffusion?

If we take a homogeneous solution and keep the different parts at the same temperature, the solution will remain homogeneous. If, on the other hand, the different parts of a homogeneous solution are kept at different temperatures, the solution will no longer remain homogeneous, but the different parts will have different concentrations — the colder parts of the solution will become more concentrated and the warmer parts more dilute. This was first observed by Ludwig[1] in 1856.

This phenomenon was thoroughly studied by Soret,[2] as has been discussed under the "Principle of Soret" (p. 75). The change in concentration, as we saw, when equilibrium is established is calculable from the law of Gay-Lussac, and the difference in concentration between the colder and the warmer parts of the solution is expressed thus. Suppose the colder part of the solution is at temperature a, and the warmer part at temperature b, the difference in concentration is $\frac{b-a}{273}$.

Osmotic Pressure Produces Diffusion. — We now come to the fundamental point in connection with diffusion. What causes it?

A dissolved substance passes from one part of a solution to another. The different parts of the solution may be widely removed from one another, one part may be very high above the other; and yet the dissolved substance will rise to the top of the solvent, as we have seen, right against the pull of gravitation.

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[1] *Wien. Ber.* **20,** 539 (1856).

[2] *Ann. Chim. Phys.* [5], **22,** 293 (1881).

It is obvious that to effect such results some force is necessary, and it must be a force of very considerable magnitude. The question is, what is this force?

On thinking over the forces which exist in solution the most obvious, as we have seen (p. 90), which might produce diffusion is osmotic pressure — does it?

This question can be answered most directly by comparing the laws of osmotic pressure with the laws of diffusion. A moment's thought will show that the law of Fick for diffusion is strictly analogous to the law of Boyle for osmotic pressure. Fick's law says that the amount of substance that will diffuse from the one solution to the other is proportional to the difference in concentration between the two solutions. Boyle's law for osmotic pressure states that the osmotic pressure at the surface of contact of two solutions, or of a solution and a solvent, is proportional to the difference in concentration of the two solutions. The two phenomena thus obey exactly the same law as far as the quantity of substance that diffuses and the amount of osmotic pressure under the same conditions are concerned.

Having found that the law of Fick for diffusion is analogous to the law of Boyle for osmotic pressure, we would naturally look farther and see whether there are any other laws of diffusion which can be compared with laws of osmotic pressure. The most obvious for such further comparisons is the law of the temperature coefficients of the two phenomena.

It will be recalled that the law of Gay-Lussac for gases was shown, from the measurements of osmotic pressure by Pfeffer, to hold approximately for solutions. The recent measurements of osmotic pressure by Morse and his coworkers have shown that this law holds approximately for osmotic pressure under all conditions, and rigidly under many conditions. The principle of Soret for diffusion shows that the law of Gay-Lussac holds at least approximately for the temperature coefficients of diffusion; and the most recent work, in which the solutions were allowed to stand for a long time, indicates that this law holds very closely or perhaps rigidly for diffusion. Two of the fundamental laws of osmotic pressure therefore apply to the phenomena of diffusion, and we would naturally conclude either that the one is the cause of the other, or that diffusion and osmotic pressure are both the results of a common cause, which at present is entirely unknown. But since we know of no such common cause we may say that the cause of diffusion is osmotic pressure.

Let us recall the order of magnitude of osmotic pressure (p. 54), and we see that we are dealing with a very large force. A normal aqueous solution of a nonelectrolyte in contact with pure water exerts an osmotic pressure of between twenty and thirty atmospheres. Many substances are so soluble that we can prepare solutions five or even ten times normal. Such solutions would, respectively, have at least one hundred and twenty-five and two hundred and fifty atmospheres of osmotic pressure, when brought in contact with the pure solvent. If the dissolved substances were electrolytes and therefore dissociated, their solutions would show still greater osmotic pressures. If the solute were a binary electrolyte each molecule would dissociate into two ions; if a ternary electrolyte, into three ions; and so on. Since, as we have seen, an ion exerts the same osmotic pressure as a molecule, such solutions, if completely dissociated, would exert two or three times the osmotic pressures of solutions of nonelectrolytes of corresponding concentrations.

We can gain from these facts some idea of the magnitude of the force which we call osmotic pressure. For solutions of any appreciable concentration, it is large; for concentrated solutions, it is enormous. This shows us why it is that dissolved substances diffuse practically independent of the relative specific gravities of solvent and solute. The driving force is so great that the relative densities of the dissolved particle and solvent are small in comparison.

Importance of Osmotic Pressure for Chemistry. — Now that we have seen that osmotic pressure is the probable cause of diffusion, we can begin to realize the importance and significance of osmotic pressure for nature, and therefore for the science of nature or natural science.

If osmotic pressure did not exist we would not have diffusion in solution. If we did not have diffusion, we could not have a homogeneous solution for any appreciable length of time, unless we kept it constantly in a violent state of agitation. It would therefore be impossible to maintain a solution standard for any time. Without standard solutions all volumetric analysis would, of course, be impossible. Without volumetric analysis much of chemistry would be changed, since there are many analytical processes that we can carry out volumetrically, but we cannot gravimetrically. Remove standard solutions from chemistry and this branch of science would be set back indefinitely.

Bearing of Osmotic Pressure on Biological Phenomena. — When we turn to biology, we find that homogeneous solutions are almost as important as for chemistry. Living matter must often be surrounded by a solution of a certain substance or of certain substances, having a concentration which is just equal to and in no case exceeds a certain value. If osmotic pressure, and consequently diffusion, did not exist, such solutions on standing would become more concentrated in some parts and more dilute in others. Those living forms which depend for their existence upon a definite concentration of certain substances, would cease to live as soon as the homogeneity of the solution was destroyed, one part becoming too concentrated for their existence, the other too dilute.

Approximate homogeneity of solution is often of fundamental importance in obtaining food. This applies especially to nonmobile animals and to plants which cannot go after their food, but which must depend upon the food being brought to them in solution. If such solutions were nonhomogeneous, being more concentrated in certain parts than in others, there would be an excess of food in certain parts and little or none in other portions of the solution. The result is obvious. Many individuals, being deprived of sufficient food, would die.

If there were no such force in a solution to produce or maintain homogeneity, those parts of a solution of foodstuffs which under one set of conditions were the more concentrated, under other conditions might contain little or no food. Those individuals which at one time might be most favorably placed with respect to food, at another time might be completely deprived of it, and, consequently, exterminated. In this way it is quite easy to conceive of a whole species being exterminated, due to the lack of a fairly homogeneous solution of food.

Then consider an even more fundamental question for living forms than that of food supply; *i.e.*, the contents of the cells themselves of which all living forms are made. These cells are often very sensitive systems. A slight disturbance either in the solutions which surround them or still more, perhaps, in their own contents, would produce death. Let us suppose that the fluids surrounding the cells, which are usually solutions of a great number of things, should no longer preserve homogeneity of concentration, but should become in some parts more concentrated and in others more dilute, then what would happen? The cell could live and function normally only when surrounded by solutions of certain substances at certain definite concentrations. The solution around the cell has now become in one part more concentrated, and in the other more dilute, than the normal. The result is obvious. The cells in the more dilute part of the solution would die because the solution was too dilute for their existence. Those in the more concentrated part of the solution would die because the solution was too concentrated for them to perform the normal functions of life. The result would be disastrous for all the cells.

Take one more step and go within the cell itself. A cell is, for our purpose, an aqueous solution of a large number of substances each usually having a pretty definite concentration: the whole surrounded by a sac. The cell is, further, a very sensitive system. *Slight disturbances* in the normal equilibrium of concentrations of the various constituents will frequently produce death.

Suppose the solutions within the cell did not remain homogeneous, but that the heavier constituents settled to the bottom, as would be the case if there were no diffusion to maintain homogeneity and no osmotic pressure to produce diffusion. The result is obvious. The cell would die.

We thus see that homogeneity of solutions, both without and within the cells, is absolutely essential to living matter. This homogeneity can, of course, be maintained only by diffusion, and diffusion is due to osmotic pressure. We thus see that osmotic pressure in solutions is *absolutely essential to life as we now know it.* Indeed, it is difficult to conceive of living matter having any close relation to life as it now exists upon the earth, without osmotic pressure in solution to maintain homogeneity of concentration.

Osmotic Pressure and Geology. — When we turn from biology to geology the effect of osmotic pressure in maintaining solutions of homogeneous concentration is hardly less important. Take, for example, the rocks that are deposited from aqueous solutions. If such solutions were not maintained more or less homogeneous by diffusion, the compositions of the various deposits from such solutions would be very different from what we now know them to be. The heavier constituents, being near the bottoms of the solutions, would tend to come down first, and the present order of such deposits would be greatly changed.

In the case of the igneous rocks the effects of heterogeneous solutions would be perhaps even more pronounced. The molten magmas, many of which, as we have seen, are true solutions, would deposit rocks of very different composition, if there were no approach to homogeneity in the composition of such magmas. If a magma, once approximately homogeneous, were to become very heterogeneous due to the absence of all diffusion, the heavier constituents of such a magma would, of course, tend to settle to the bottom of the fused mass, and when this had become sufficiently cool, would solidify and form rocks of very different composition from those now known to us as having been deposited from such magmas.

Without diffusion and its cause, osmotic pressure, the composition of the rocks would be very different from what it is, and the rocks are the elements of geology.

CHAPTER VII

DEPRESSION OF THE VAPOR-TENSION OF A SOLVENT BY SUBSTANCES DISSOLVED IN IT

It has long been known that, in general, when solids are dissolved in liquids, the vapor-tensions of the latter at any given temperature are reduced. When liquids are dissolved in liquids the same phenomenon manifests itself, provided the boiling-point of the liquid solute is considerably higher than that of the solvent.

Work of Faraday. — The first to have investigated this phenomenon quantitatively was Michael Faraday, all things considered, one of the very greatest experimenters who has ever lived. In 1822 he published a paper[1] on the "Temperature Produced by the Condensation of Vapor." He determined the boiling-points of saturated solutions of a number of salts: acid potassium carbonate, potassium tartrate, ammonium chloride, etc. From his work Faraday[2] concluded that "the temperature of aqueous vapor from a saline solution is always 100°, whatever the boiling-point of the solution under atmospheric pressure."

The editor, Gay-Lussac,[3] makes the following comment, which, when we consider the men involved, has a particular interest.

"It would be very difficult to conceive of the vapor given off from the surface of a salt solution, not having exactly the same temperature as the solution from which it came. Without introducing any theory, we can state from the irrefutable evidence of experiment that *the temperature of the vapor from any liquid whatever, under any pressure whatever, is exactly equal to that of the layer of liquid imme-*

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[1] *Ann. Chim. Phys.* [2], **20**, 320 (1822).

[2] *Ibid.*, 325.

[3] *Ibid.*, 325.

diately in contact with the vapor. If this fact escaped Faraday, we are convinced that it is because he had not made a sufficiently large number of experiments, and had not worked with a sufficiently sensitive thermometer."

Investigations of Wüllner. — The next work in this field of special interest and significance is that of Wüllner,[1] which was done between three and four decades after that of Faraday.

A few of the results obtained by Wüllner will serve to illustrate the relation discovered by him. If we represent the vapor-pressure of pure water by P, the lowering of the vapor-pressure of 100 parts of water by one part of salt by P_1, we have the following relations. Wüllner's results for only one salt, sodium chloride, will be given.

	P	5%	10%	20%	30%	P_1	$\frac{P_1}{P}$
Temperature	mm.	mm.	mm.	mm.	mm.	Mean	
19.9°	17.28	0.98	1.47	—	4.06	0.149	—
35.0°	41.82	1.79	3.11	—	8.13	0.300	0.0072
49.8°	91.09	2.84	5.81	11.36	18.20	0.620	0.0068
64.8°	185.27	—	9.88	21.45	—	1.090	0.0059
82.2°	388.33	—	21.58	46.20	—	2.240	0.0058
100.5°	775.40	—	44.90	92.41	—	4.450	0.0057

We see from the above table that $\frac{P_1}{P}$ is practically constant, if we consider the comparatively large experimental errors involved in the results. From his study of a fairly large number of salts Wüllner generalized his results as follows:

"The lowering of the vapor-pressure of water by dissolved substances is proportional to the amounts of substances in the solution."

This conclusion was called in question about twenty years later by Pauchon,[2] and Tammann[3] confirmed the validity of Pauchon's objection. The latter showed that the so-called law of Wüllner was only an approximation.

Study of Vapor-Tension by Walker. — The next really important investigation in this field is that of Walker,[1] carried out in 1888 in the laboratory of Ostwald in Leipzig.

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[1] *Pogg. Ann.*, **103**, 529 (1858); **105**, 85 (1858); **110**, 564 (1860).

[2] *Compt. Rend.*, **89**, 752 (1879).

[3] *Wied. Ann.*, **24**, 523 (1885).

His method of work was probably the best that had been used up to that time, and is interesting. A few words concerning it are worth while.

The problem was to compare directly the vapor-tension of water with that of an aqueous solution. The apparatus was very simple, consisting of three ordinary Liebig bulbs, such as are used in the combustion analysis of organic compounds and a U-tube. The solution was introduced into two of the bulbs, while the third contained the pure solvent. Fragments of pumice stone moistened with sulphuric acid were added to the U-tube.

Air dried by sulphuric acid was drawn slowly through the whole system. In passing through bulbs one and two the air was saturated with water-vapor at the tension of the vapor over the solution. When this air was drawn through bulb three it took up more water-vapor, since the tension of the vapor of water was greater over the pure solvent than over the solution. The air was then passed through the U-tube containing sulphuric acid and dried to the same degree as when it entered the first tube filled with the solution.

The loss in weight of the two tubes containing the solution was then determined. The loss in weight of the tube containing the pure solvent was also determined. The gain in weight of the tube containing the sulphuric acid must be exactly equal to the total losses in the weights of the other three tubes. From the amount of water lost by the solution, and the amount lost by the pure solvent, we can calculate directly the lowering of the vapor-tension of the solvent produced by the dissolved substance.

A few of the results obtained by Walker[2] will be given. The number of parts salt to 100 parts water in the column under g; c is the relative lowering of vapor-pressure produced by one molecule of substance in 100 molecules of water.

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[1] *Zeit. phys. Chem.*, **2**, 602 (1888). [2] *Ibid.*, **2**, 604 (1888).

	g	c
NaCl	5.96	2.07
NaCl	18.60	2.18
NaCl	32.265	2.29
KCl	7.66	2.02
$NaNO_3$	8.791	1.97
$CaCl_2$	11.386	3.30
$MgCl_2$	4.791	3.57
$MgCl_2$	9.691	4.01
$BaCl_2$	21.443	3.00
$SrCl_2$	16.002	3.28

One conclusion is justified from these results. Where more than one concentration of a substance was studied, the more concentrated the solution the greater the relative lowering of the vapor-tension. This fact is of importance in connection with a theory of solution which will be developed in the last chapters of this book.

This brings us to the most important series of investigations that has thus far been carried out on the vapor-tensions of solutions and solvents; viz., the work of Raoult.

Raoult and the Vapor-Tensions of Solvents and of Solutions. — The earlier workers in this field had studied aqueous solutions almost exclusively. This we know today was unfortunate, and for two independent reasons. In the first place, water at ordinary temperatures has comparatively small vapor-tension, and on account of its small molecular weight the depression of its vapor-tension by dissolved substances is very small. We are then measuring a small change in a small quantity, and the experimental error is, of course, relatively large.

Further, as we have seen, water is one of the best dissociating solvents. This means that electrolytes dissolved in this solvent are largely broken down into ions. Any relations between the lowering of the vapor-tension and the concentration of the solution which might exist, would in aqueous solution be liable to be masked by the breaking down of the molecules into ions by this solvent.

Raoult[1] fortunately turned to nonaqueous solutions and the result was the discovery of certain relations of fundamental significance. Ether is a solvent which has a high vapor-tension even at ordinary temperatures. With this solvent the quantity to be measured is relatively large, and the error of measurement therefore relatively small. Further since ether has a comparatively large molecular weight, the lowering of its vapor-tension by dissolved substances is relatively great, as we shall see. It was therefore an ideal solvent with which to study vapor-tensions of both solvent and solutions.

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[1] *Ann. Chim. Phys.* [6], **15**, 375 (1888).

The experimental work of Raoult is admirable for its insight into sources of experimental error and ingenuity in overcoming or correcting for these errors. The method employed was the barometric. The solvent or solution was introduced into a glass tube over mercury and the pressure determined from the depression of the mercury column. The observed depression was corrected for a number of conditions — for the pressure of the liquid on the column of mercury beneath it; for the concentrating of the solution at and near its surface, due to the loss of the solvent as vapor; and for a number of other errors, but for these, reference must be had to the original paper. Let us now see what Raoult found.

Raoult's Results — Effect of Concentration. — Raoult took up first the effect of *concentration* of the solution on the vapor-pressure of solutions in ether. If we represent by O the number of grams of solute in 100 grams of solvent; by N, the number of molecules of solute in 100 molecules of solvent, readily calculated from O, knowing the molecular weights of solute and solvent; by R, the ratio between the molecular weights of solute and solvent multiplied by 100; we have, for solutions of oil of turpentine in ether the following results.[1]

O	N	R Observed	R Calculated
10.2	5.9	94.0	94.7
20.2	12.1	88.1	89.1
35.9	23.4	78.1	78.9
50.3	35.5	67.6	68.0
62.8	47.9	56.2	56.9
76.9	64.5	42.1	42.0

[1] Taken from *Ann. Chim. Phys.* [6], **15**, 388 (1888).

The values in the last column are calculated from the equation

$$\frac{f'}{f} = 1 - K \times \frac{74 \times p'}{74 \times p' + pm}$$

in which f' is the vapor-pressure of the solution, f, that of pure ether, p', the weight of the dissolved substance, p, the weight of the ether, m, the molecular weight of the dissolved substance, and 74 the molecular weight of ether; K a coefficient whose value depends upon the nature of the solute.

The agreement between the observed and calculated values is surprisingly good. Equally satisfactory agreements between observed and calculated values were found for nitrobenzene in ether, aniline in ether, etc.

The value of the coefficient K for various substances dissolved in ether is very nearly constant, as the following results will show.

Oil of turpentine	$K = 0.90$
Aniline	$K = 0.90$
Ethyl benzoate	$K = 0.90$
Methyl salicylate	$K = 0.82$
Nitrobenzene	$K = 0.70$

For other solvents K is only a little less than unity.

Having formulated the effect of concentration on the lowering of the vapor-tension of solvents by dissolved substances, Raoult raised and answered the question as to the *effect of temperature* on the relative lowering of the vapor-tension of ethereal solutions.

Effect of Temperature. — Raoult dissolved four high-boiling substances in ether, and measured carefully the vapor-pressures above these solutions at different temperatures. The range of temperature was from 0° to 21°. The following results were obtained by him, f being the vapor-tension of the solvent, and f' that of the solution.[1]

27.601 GRAMS HEXACHLORETHANE IN 100 GRAMS ETHER

Temperature	f	f'	$\frac{f'}{f} \times 100$
1.0°	197.0	181.3	92.0
3.7°	224.2	205.4	91.6
18.8°	418.6	280.9	91.0
21.0°	457.3	417.8	91.4

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[1] Taken from *Ann. Chim. Phys.* [6], **15**, 388 (1888).

The variation of $\frac{f'}{f}$ from a constant is scarcely greater than the experimental error, over the temperature range 0° to 21°.

Effect of Nature of Dissolved Substance. — The most important question still remains — the effect of the *nature of the dissolved substance* on the lowering of the vapor-tension of ether. Raoult deduced the following very simple and important relation: if we represent the vapor-tension of ether by f, and of ethereal solutions by f', the number of molecules of solute in 100 molecules of solution by N, we have,

$$\frac{f'}{f} \times 100 = 100 - KN$$

or,

$$\frac{f - f'}{f} = \frac{KN}{100}$$

The quantity $\frac{f-f'}{f}$ is called by Raoult the "relative diminution of vapor-pressure." Raoult formulated this relation as follows:

"For ethereal solutions the relative diminution of vapor-pressure is proportional to the number of molecules of non-volatile substance in 100 molecules of the solution."

For dilute solutions, K, as we have seen, is very nearly 1.0, when the above expression becomes,

$$\frac{f - f'}{fN} = 0.01$$

Raoult tested this deduction by dissolving a number of substances in ether, with the following results.[1]

	$\frac{f-f'}{fN}$
Oil of turpentine	0.0099
Methyl salicylate	0.0094
Benzoic acid	0.0097
Aniline	0.0106

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[1] *Ann. Chim. Phys.* [6], **15**, 400 (1888).

Effect of Nature of Solvent — Generalization of Raoult. — Raoult had thus shown that the lowering of the vapor-tension of ether is dependent only on the ratio between the molecules of the solvent and of the dissolved substance, and is practically independent of the nature of the dissolved substance. There still remained, however, one more fundamental question. Is the relative lowering of the vapor-tension dependent upon, or independent of the *nature of the solvent?*

This question was answered very satisfactorily by Raoult, in another paper.[1] He measured the lowering of the vapor-tension of twelve solvents by different substances dissolved in them, and from the results calculated the following relations.

Let M be the molecular weight of the solvent and K the molecular lowering of its vapor-pressure, the ratio $\frac{K}{M}$ is the relative lowering of vapor-pressure produced by one molecule of solute in one hundred molecules of the solvent, regardless of the nature of both solute and solvent. His results for a few solvents are given below.

Solvent	M	K	$\frac{K}{M}$
Water	18.	0.185	0.0102
Carbon disulphide	76.0	0.80	0.0105
Chloroform	119.5	1.30	0.0109
Benzene	78.0	0.83	0.0106
Ether	74.0	0.71	0.0096
Acetone	58.0	0.59	0.0101
Methyl alcohol	32.0	0.33	0.0103

Raoult points out that although the values of K and of M vary as much as one to nine, the ratio between the two is very nearly constant, the constant having the approximate value of 0.0105.

Raoult then formulates what has come to be known as "the Law of Raoult," which is a generalization that is independent of the chemical nature both of the solvent and of the dissolved substance.[2]

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[1] *Compt. Rend.*, **104,** 1430 (1887).

[2] *Compt. Rend.*, **104,** 1433 (1887).

"A molecule of any non-volatile solid other than salts in solution in one hundred molecules of any volatile liquid, produces a lowering of the vapor-tension of the solvent which is nearly a constant part of the value of this quantity — the constant being very nearly 0.0105."

This generalization, which we now know holds only approximately, enables us, as Raoult pointed out, to use this property of solutions to determine the molecular weight of the dissolved substance. Another method based upon the same principle as this, is, however, so far to be preferred that this application of the lowering of vapor-tension will only be referred to.

Raoult followed one lead after another, first studying the effect of the dissolved substance and arriving at a partial generalization; then the effect of the solvent, and completing the generalization which shows that lowering of vapor-tension, like osmotic pressure, is a property which depends upon numbers, and numbers only — the ratio between the number of parts of the solvent and of the dissolved substance. This work of Raoult, from the standpoint of method, as well as of bearing on modern chemical thought, is to be ranked among the classics of chemistry.

Method of Frazer and Lovelace for Measuring Vapor-Tension. — This method[1] applied to the vapor-pressures of aqueous solutions is a differential, static method. It consists in measuring directly the difference between the vapor-tension of the pure solvent and that of the solution, by means of a very sensitive manometer designed by Lord Rayleigh for the study of the behavior of gases at low pressure.

The study of the vapor-pressure of solutions by the static method necessitated special precautions to eliminate error due to: (1) temperature changes, (2) changes in the surface concentration of the solution, and (3) incomplete removal of dissolved gases from the solvent and from the solution. The first source of error is practically removed by using a thermostat capable of such accurate control, that the variations in temperature cannot be detected by a Beckmann thermometer reading to 0.001° C.

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[1] *Journ. Amer. Chem. Soc.*, **36**, 2439 (1914); *Zeit. phys. Chem.*, **89**, 155 (1914).

The error due to change in surface concentration is eliminated by vigorous and continuous stirring in a vacuum of both solution and solvent.

Traces of dissolved gases are removed by allowing the vapor from the solution and solvent to expand into an exhausted flask. The operation is repeated again and again, allowing sufficient time at each exhaustion for the space to become saturated with the dissolved gases.

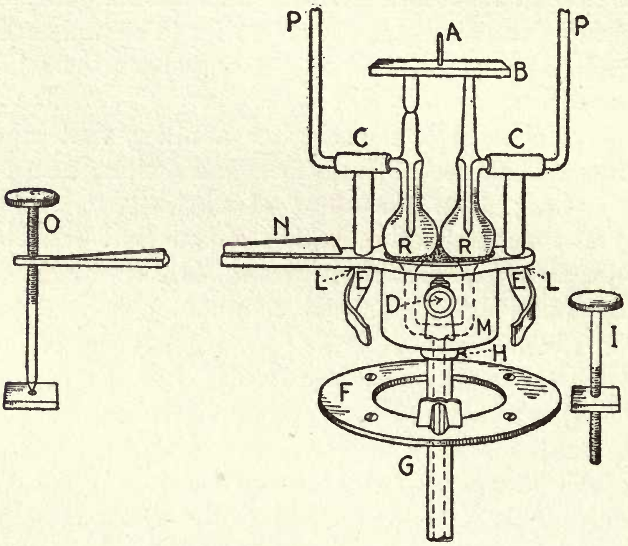

Fig. 2.

To avoid the leakage of air into the apparatus all connections are sealed and no stopcocks are used.

The measurement of the difference in the vapor-pressure of solution and of solvent is made by means of the Rayleigh manometer shown in figure 2. It consists of a Y-shaped glass tube. On each of the upper limbs is blown a bulb about 40 mm. in diameter. The lower limb of the Y tube is of barometric height and to its end is attached a mercury reservoir, the height of which can be accurately adjusted by turning the screw *I* shown to the right of the apparatus. The glass Y tube is set with plaster of Paris in an iron pot *M*. *M* is pivoted at *D*, and the instrument may be rotated on *D* by means of the screw *O*.

When the apparatus is exhausted the mercury rises into the two limbs of the Y tube. By proper manipulation of *I* and *O*, the two ground-glass points *RR* are made just to touch their images in the mercury, coincidence being determined by means of two microscopes (not shown in the drawing). At *CC* two glass tubes *PP* are sealed. One of these connects one limb of the Y with a glass bulb containing air-free solvent, and the other in like manner connects the other limb with the vessel containing the solution. The bulbs containing the solution and solvent are immersed in the thermostat bath mentioned above.

When the apparatus is completely exhausted, or when the same pressure exists in the two limbs of the Y tube, and the adjustment of the points made as mentioned above, the instrument is in the zero position, the points being exactly at the same height. When there is a difference in pressure on the two sides, as when one of the tubes *P* communicates with the solution and the other with the pure solvent, the mercury surface is depressed more in the limb in which the greater pressure is exerted, and it is necessary to rotate the instrument by means of *O* a certain amount in order to bring both points *RR* into coincidence again with their images. The amount of this rotation from the zero position is determined by means of the metallic mirror *A*, mounted directly on the instrument, and a telescope and scale mounted about three meters in front of *A*. Having determined the amount of rotation from the zero position, and knowing accurately the distance between the points *RR*, and the distance from *A* to the scale, the difference in the level of the points can be readily calculated. This is the depression of the vapor-tension of the solvent by the dissolved substance in millimeters of mercury, which is the quantity desired.

A few of the results obtained by Frazer and Lovelace are given below.

VAPOR-PRESSURE LOWERINGS OF SOLUTIONS OF MANNITE AT 20°

Concentration	Observed lowering
0.1 normal	0.029 mm Hg.
0.2 "	0.059 " "
0.3 "	0.090 " "
0.4 "	0.118 " "
0.5 "	0.153 " "

VAPOR-PRESSURE LOWERINGS OF SOLUTIONS OF POTASSIUM CHLORIDE AT 20°

Concentration	Observed lowering
0.2 normal	0.110 mm. Hg.
0.4 "	0.217 " "
0.6 "	0.329 " "
1.0 "	0.547 " "
1.5 "	0.826 " "
2.0 "	1.102 " "

Other investigators have recently developed methods for measuring the vapor-tensions of solvents and of solutions, but reference[1] only can be made to their work.

The Boiling-Point Method. — The vapor-tension of most solvents at ordinary temperatures is small and the lowering of this tension by dissolved substances is a small part of this small quantity, as we have seen. The measurement of a very small quantity is always difficult, and unless some very refined method such as that of Frazer and Lovelace is employed, the experimental error is relatively large. For general practical use in the laboratory such methods are not adapted; and it is important to know the molecular weights of substances in general, in solvents in general. For this purpose the vapor-tension method has been abandoned in favor of a method based upon the same principle, but which is incomparably simpler to apply.

The vapor-tension method depends upon heating the solution and the solvent to the same temperature, and measuring the vapor-tensions of the two at the constant temperature.

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[1] Tower: *Journ Amer. Chem. Soc.*, **30**, 1219 (1908); Mündel: *Zeit. phys. Chem.*, **85**, 435 (1913); Washburn and Heuse: *Journ. Amer. Chem. Soc.*, **37**, 309 (1915).

Instead of keeping the temperature constant and measuring the different vapor-pressures at this constant temperature, we can heat the solution and the solvent until the vapor-pressures of the two are equal, and then measure the temperatures required to bring about this condition. The constant pressure chosen is the pressure of the atmosphere, and the temperatures are the boiling-points of solution and solvent; *i.e.*, the temperatures necessary to produce vapor over both solution and solvent which will just overcome the atmospheric pressures. The vapor-tension method thus becomes the "boiling-point method."

Boiling-point Method of Beckmann. — The first to devise a reasonably satisfactory method for determining the boiling-points of solutions and solvents was Beckmann. The essential features of any good boiling-point method are a very sensitive thermometer, and good heat insulation around the boiling liquid. The thermometer devised by Beckmann has a very large bulb, and also a very fine capillary, but the peculiar feature of it is at the top. It is provided here with a reservoir. By proper manipulation, more or less of the mercury from the bulb may be transferred to this reservoir so as to adjust the reading of the thermometer on the scale for widely different temperatures. The Beckmann thermometer is therefore a purely differential thermometer.

Beckmann[1] has designed a large number of forms of apparatus for determining the boiling-points of solutions and of solvents. All are based upon the same principle. The liquid whose boiling-point is to be determined is placed in a glass vessel of test-tube shape, and this is surrounded by an asbestos jacket or a vessel containing some of the same liquid heated to boiling. The thermometer is plunged directly into the liquid. All of these forms appear to the writer to have one serious defect — they do not adequately prevent the cold, recondensed solvent from coming in contact with the thermometer before it has been reheated to its true boiling-point, and they do not sufficiently safeguard the apparatus and thermometer from the effects of radiation. To overcome, as far as possible, these objections the following form of boiling-point apparatus was designed by the author.

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[1] See the Author's *Elements of Physical Chemistry*, 4th edition (The Macmillan Co.), p. 263.

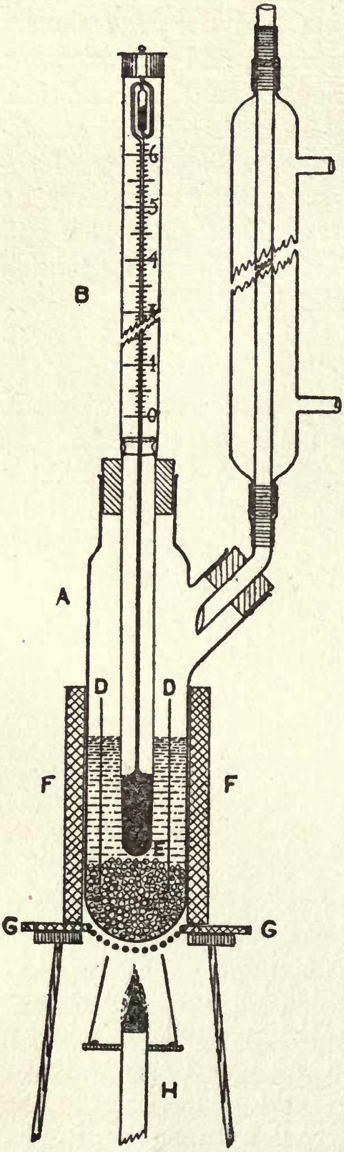

FIG. 3.

Boiling-Point Apparatus of Jones. — The apparatus designed by Jones[1] is sketched in figure 3. It is simply a glass tube with glass beads and platinum scraps in the bottom and a condenser attached; a platinum cylinder *D* being introduced as shown in the figure; the object of the metal cylinder being, in the first place, to cut off the colder, recondensed solvent from the bulb of the thermometer, until the liquid has been heated again to the boiling-point. This colder liquid must pass down through the entire length of the boiling liquid before it can enter the cylinder from below, and, consequently, is heated again to the boiling-point.

The platinum cylinder serves also to reduce to a minimum the effect of direct radiation. If the warm bulb of the thermometer is not surrounded completely by metal, it will radiate heat outward through the liquid to colder objects in the neighborhood; liquids being somewhat transparent to the longer heat rays. This effect is reduced to a minimum by surrounding the thermometer bulb with metal heated to the same temperature as the bulb of the thermometer itself. On top of the beads in the bottom of the glass vessel a few scraps of platinum are placed, to prevent the radiation of heat directly from the flame to the bulb of the thermometer.

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[1] *Amer. Chem. Journ.*, **19**, 581 (1897).

Beckmann, in his later forms of apparatus, surrounded the tube containing the liquid to be boiled with a double-walled vessel containing between its two walls some of the same liquid whose boiling-point was to be determined. This was boiled at the same time that the liquid in the inner cylinder was boiled. In this way the effect of radiation was somewhat diminished, but by no means rendered negligible. The platinum cylinder accomplishes both of the purposes for which it was introduced, as is shown by the results which have been obtained with this form of apparatus.

Molecular Weights from Boiling-Point Determinations. — It is obvious that any property which depends only on the ratio between the number of parts of solute and solvent — an arithmetical property — is independent of the chemical nature of either and can be used to determine the molecular weights of substances in general, dissolved in solvents in general.

A large amount of work has been done on the molecular weights of a great variety of substances in a large number of solvents. The results of this work can be easily summarized. Substances in general in solvents in general are in the *simplest molecular condition* — *i.e.*, dissolved substances are in the same state of aggregation as gases. This doubtless has something to do with the relations discussed earlier between solutions and gases.

There are, however, many exceptions known to the above general relation. Certain substances in certain liquids are polymerized, and in some cases very much polymerized, just as certain elements and compounds in the form of vapor are polymerized. Acetone is a solvent which has very marked polymerizing power, and there are many other examples of a similar nature. It should be noted that there is no relation known between the molecular weight of a dissolved substance, and that of the same substance in the pure, homogeneous state.

Electrolytic Dissociation Measured by the Boiling-Point Method. — Another application of the boiling-point method, which in some respects is more important than the problem of molecular weights in solution, is the measurement of electrolytic dissociation in nonaqueous solvents. This was at one time very important, because we had then absolutely no method for measuring electrolytic dissociation in a large number of solvents, other than the boiling-point method, for reasons which will appear in the proper place. The boiling-point method of Beckmann could not be used for this purpose, because it was too inaccurate. An improved boiling-point method has been applied to this problem.

Jones,[1] using the apparatus designed by himself, has measured the dissociation of several salts in methyl and in ethyl alcohols. Theoretically the matter is very simple. From the rise in the boiling-point produced by dissolving a known weight of substance in a known weight of solvent, the rise produced by dissolving a gram-molecular weight of the substance in 1000 grams of the solvent was calculated. This is known as the "molecular rise." The molecular rise for the substance in question divided by the constant for the solvent in question gives what is known as the Van't Hoff coefficient "i," since it is the coefficient which was introduced into the simple gas equation $PV = RT$ to make it apply to the osmotic pressures of electrolytes.

The dissociation λ for binary electrolytes or those which break down into two ions each is,[2] $\lambda = i - 1$.

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[1] *Zeit. phys. Chem.*, **31**, 114 (1899).

[2] *Ibid.*, **11**, 110, 529; **12**, 639 (1893).

For ternary electrolytes or those whose molecules break down into three ions each, $\lambda = \frac{i-1}{2}$ and so on.

A few of the results obtained in this laboratory[1] are given in the following table.

	Conc	Dissociation in methyl alcohol	Dissociation in ethyl alcohol
KI	0.1	52.0 %	25.0 %
NaI	0.1	60.0 "	33.0 "
NH_4I	0.1	50.0 "	....
KBr	0.1	50.0 "	....
NH_4Br	0.2	49.0 "	21.0 "
CH_3COONa	0.1	38.0 "	14.0 "

These results are, of course, to be regarded only as approximations, the error in the most refined boiling-point method being considerable, if for no other reason, because the boiling-point of a solvent is affected so markedly by slight changes in the barometer.

Molecular Weights of the Metals in Mercury. — Before leaving the subject of vapor-tension, there is one other application of this method of determining molecular weights which must be considered.

Ramsay[2] in 1899 studied the lowering of the vapor-tension of mercury by metals dissolved in it. Knowing the vapor-tension constant of mercury and the concentration of the amalgam in question, he could calculate the molecular weight of the metal in question in the mercury, under the conditions of the experiment. A few of his results, taken from the paper referred to above, are given.

Metal	Number of atoms per 100 atoms Hg.	Molecular weight	Atomic weight
Li	1.70	7.1	7.02
Na	0.86	21.6	23.04
Na	1.87	18.3	23.04
Na	5.35	15.1	23.04
K	1.55	29.1	39.14
K	5.26	30.2	39.14
Ca	0.19	19.1	40.08
Ba	0.90	75.7	137.00
Mg	0.70	24.0	24.30
Mg	4.82	21.5	24.30
Mn	1.14	55.5	55.00
Au	1.59	207.4	197.22
Au	2.80	208.1	197.22

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[1] Taken from *Ibid.*, **31**, 140 (1899).

[2] *Journ. Chem. Soc.*, **55**, 521 (1889).

The above results contain a number of points of interest. Most of the metals dissolved in mercury are in the simplest atomic condition. There are, however, some exceptions, and these are the interesting features.

The molecular weight of sodium is less than its atomic weight, and this becomes still smaller as the concentration of the sodium is increased.

The most remarkable results in mercury as the solvent were obtained with calcium and barium. When dissolved in mercury their *molecular weights are almost exactly half of their atomic weights.* If we consider that the amalgams of these metals studied by Ramsay were very dilute, and the experimental error therefore larger, we would not be inclined to lay so much stress upon these data, had they not to a large extent been confirmed by subsequent results by an entirely different method.

Humphrey and Mohler,[1] working with Rowland, studied the displacement of the spectrum lines, when the incandescent, elementary gases producing them were under pressure. They found that from the[2] "product of the cube root of the 'atomic volume' and the coefficient of linear expansion of the substance in the solid form, certain numbers were obtained whose ratios were the same as those of the shift for the respective elements."

The atomic volume is the atomic weight divided by the specific gravity or density in the solid state. When the displacement of the calcium lines were measured, and the results compared with the displacement calculated from the above relation, the two would agree for calcium only when the assumption was made that the atomic weight of this element in its highly heated vapor was not 40, but a smaller value.

The same result was then reached by Ramsay when certain metals are dissolved in mercury at comparatively low temperatures, and by Humphreys and Mohler, when the metals are volatilized in the electric arc.

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[1] *Astrophysical Journal,* **3,** 114 (1896).

[2] *Ibid.,* **3,** 131 (1896).

At the time that these observations were made they were very surprising. We had been accustomed to think of the chemical atoms as ultimate units which could not be broken down into anything simpler. Now in the light of the work of Thomson this conclusion is not so surprising. We know that the atoms are complex, and there is no *a priori* reason why they should not yield simpler things. Indeed, electrons have been obtained from many of them.

CHAPTER VIII

DEPRESSION OF THE FREEZING-POINT OF A SOLVENT BY THE SOLUTE

THAT dissolved substances lower the freezing-point of the solvent has been known qualitatively for a very long time. The first to have made quantitative measurements in this field seems to have been Blagden.[1] As early as 1788, he found that the amount of the lowering of the freezing-point is proportional to the amount of dissolved substance in a given volume of the solution.

Investigations of Raoult. — Very little real progress was made in the study of freezing-point lowering from the time of Blagden, until the problem was taken up by the one who, we have seen, did such magnificent work in connection with the lowering of vapor-tension of solvent by dissolved substance — Raoult.

Coppet,[2] nearly one hundred years after Blagden, did make one advance of some consequence in the study of freezing-point lowering, in that he expressed his concentrations in terms of molecular quantities, and thus made the results with different substances comparable with one another. Coppet consequently discovered that correlated substances produce essentially the same lowering of the freezing-point of water.

Raoult[3] attacked the problem of lowering of freezing-point in much the same way that he had attacked the question of lowering of vapor-tension. Instead of limiting his investigations to water as a solvent, he extended them to a fairly large number of solvents — acetic acid, formic acid, benzene, nitrobenzene, ethylene bromide. This was obviously the scientific way to proceed. Otherwise, relations holding for one or for several solvents might be discovered which would have no significance when still other solvents were brought within the scope of the work. A few of the results obtained by Raoult in the different solvents will be given.

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[1] *Phil. Trans.*, **78,** 277 (1788).

[2] *Ann. Chim. Phys.* [4], **23,** 366 (1871); **25,** 502 (1872); **26,** 98 (1872).

[3] *Ibid.* [5], **28,** 133 (1883); [6], **2,** 66 (1884).

Raoult called the lowering of the freezing-point produced by one gram of substance in one hundred grams of solvent, the "coefficient of lowering" of the substance in question. This he represented by A. M is the molecular weight of the dissolved substance, and T the molecular lowering of the freezing-point. We have,

$$MA = T$$

RESULTS OBTAINED BY RAOULT[1]
SOLVENT ACETIC ACID

Substance dissolved	Formula	Molecular lowering $MA = T$
Chloroform	$CHCl_3$	38.6
Carbon tetrachloride	CCl_4	38.9
Naphthalene	$C_{10}H_8$	39.2
Aldehyde	C_2H_4O	38.4
Benzoic acid	$C_7H_6O_2$	43.0
Ethyl alcohol	C_2H_6O	36.4
Hydrochloric acid	HCl	17.2
Sulphuric acid	H_2SO_4	18.6

From the results of the study of about sixty compounds in this solvent, Raoult concluded that the molecular lowerings in acetic acid approach two numbers — 39 and 18; the one being approximately the half of the other.

In formic acid the following results were obtained:

Substance dissolved	Formula	Molecular lowering $MA = T$
Chloroform	$CHCl_2$	26.5
Benzene	C_6H_6	29.4
Ether	$C_4H_{10}O$	28.2
Acetic acid	$C_2H_4O_2$	26.5
Arsenic trichloride	$AsCl_3$	26.6
Magnesium formate	$(HCO_2)_2Mg$	13.9

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[1] Taken from *Ann. Chim. Phys.* [6], **2**, 71 to 84 (1884).

The molecular lowerings in formic acid approach the two values 28 and 14.

The molecular lowerings in benzene are grouped around 49 and 25. Similarly, the molecular lowerings in nitrobenzene group themselves around 73 and 36; and in ethylene bromide around 118 and 58.

A few of the results in nitrobenzene are given.

Substance dissolved	Formula	Molecular lowering $MA = T$
Chloroform	$CHCl_3$	69.9
Carbon disulphide	CS_2	70.2
Naphthalene	$C_{10}H_8$	73.6
Ether	$C_4H_{10}O$	67.4
Acetone	C_3H_6O	69.2
Stannic chloride	$SnCl_4$	71.4
Methyl alcohol	CH_4O	35.4
Ethyl alcohol	C_2H_6O	35.6
Acetic acid	$C_2H_4O_2$	36.1

Here again we have the two sets of values, one of which is just about half the other.

Raoult studied about one hundred compounds in water, and a few of his results for aqueous solutions are given.

Substance dissolved	Formula	Molecular lowering $MA = T$
Hydrobromic acid	HBr	39.6
Phosphoric acid	H_3PO_4	42.9
Sodium hydroxide	$NaOH$	36.2
Potassium chloride	KCl	33.6
Sodium nitrate	$NaNO_3$	34.0
Calcium hydroxide	$Ca(OH)_2$	48.0
Calcium chloride	$CaCl_2$	49.9
Strontium nitrate	$Sr(NO_3)_2$	41.2
Sulphurous acid	H_2SO_3	20.0
Boric acid	H_3BO_3	20.5
Methyl alcohol	CH_4O	17.3
Dextrose	$C_6H_{12}O_6$	19.3
Formic acid	H_2CO_2	19.3
Urea	CON_2H_4	17.2

The values for water produced by compounds which are dissociated are around 37; the other class of values is around 18.5.

What is the meaning of the two values in any given solvent? Raoult points out that in a constant weight of any solvent all of the physical molecules, independent of their nature, produce the same lowering of the freezing-point. He attempts to interpret the two values found for every solvent in the light of this idea. When the maximum molecular lowering is produced it means that the physical molecule contains one of the simplest chemical molecules of the substance — the two are identical. When some of the chemical molecules are united in pairs, the molecular lowering is less than the maximum. When all the chemical molecules are united in pairs, the molecular lowering is just *half the maximum*. The molecular lowering of water is sometimes *less than half* the maximum. This means, according to Raoult, that the chemical molecules are, in part at least, aggregated in groups of three to form the physical molecules, which is the unit in determining the lowering of the freezing-point of a solvent.

Raoult explains thus the results with *different compounds* in the same solvent, but this does not explain the results with the *same compound* in *different* solvents; which is, of course, necessary before any comprehensive generalization can be reached.

Before this can be done, we must calculate the results in the different solvents on a comparable basis. This is most easily accomplished by referring the results to one molecule of solute in 100 molecules of solvent. To do this it is only necessary to divide the molecular lowering for each substance T, by the molecular weight of the solvent M.

If we represent the lowering produced by one molecule of substance in 100 molecules of solvent, by T', we have

$$T' = \frac{T}{M}$$

In the following table are the results for six solvents, T being the maximum molecular lowering of the freezing-point.[1]

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[1] Taken from *Ann. Chim. Phys.* [6], **2**, 91 (1884).

Solvent	M	T	$\frac{T}{M}$
Water	18	47	2.61°
Formic acid	46	29	0.63
Acetic acid	60	39	0.65
Benzene	78	50	0.64
Nitrobenzene	123	73	0.59
Ethylenebromide	188	119	0.63

Omitting water, the ratio T' is very nearly constant, varying only between 0.59° and 0.65° — the mean being 0.63°.

Raoult would explain the apparent abnormality presented by water as follows. If we assume that the physical molecule of water is made up of three of the simplest chemical molecules, we can explain all of the molecular lowerings of this solvent, which are in the neighborhood of 37.

$$\frac{37}{18 \times 3} = 0.685.$$

More recent work, however, gave molecular lowerings of water which are as great as 47. To account for this value, we must assume that *the physical molecule of water is made up of four of the simplest chemical molecules.*

$$\frac{47}{18 \times 4} = 0.65$$

which is very nearly the mean for the other solvents — 0.63.

It is interesting to note that this assumption of Raoult, that the molecular weight of water at zero degrees is $(H_2O)_4$, has subsequently been confirmed by the work of Ramsay and Shields,[1] on the molecular weights of pure liquids. They found that the formula of water at and near zero degrees is $H_8O_4 = (H_2O)_4$.

Raoult's Law of Freezing-Point Lowering. — Explaining the apparent abnormalities in freezing-point lowering, as Raoult did, as due on the one hand to polymerization of the molecules of the solute, and on the other to polymerization of molecules of the solvent, he was able to work out his now famous general law of freezing-point lowering.

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[1] *Zeit. phys. Chem.*, **12**, 433 (1893).

One molecule of any substance dissolved in one hundred molecules of any solvent lowers the freezing-point of the solvent nearly a constant amount, which is about 0.63°.

This law, as we shall see, lies at the basis of all subsequent work done in this field. This investigation by Raoult, like the corresponding one in the field of the lowering of vapor-tension, has become one of the classics of modern chemistry.

The Freezing-Point Method of Beckmann. — The first to devise a fairly satisfactory method for measuring the freezing-points of solvents and of solutions was Beckmann, who, it will be recalled, also devised the first reasonably satisfactory boiling-point method.

The key to the freezing-point, as to the boiling-point method of Beckmann, is his thermometer, which has already been described (p. 115). The remainder of his apparatus consists of two test-tubes, one placed within the other — the air-space between the two being from one to two centimeters wide. The Beckmann thermometer is inserted into the innermost tube, and the whole placed in a suitable freezing-mixture. The liquid around the thermometer is provided with a convenient stirrer. The air-space between the two test-tubes is for the purpose of protecting the liquid to be frozen and the thermometer immersed in it, from a too rapid lowering of temperature and from sudden changes in temperature. With this apparatus, a sketch of which is given in figure 4, Beckmann determined the molecular weights of a large number of substances in a fairly large number of solvents.

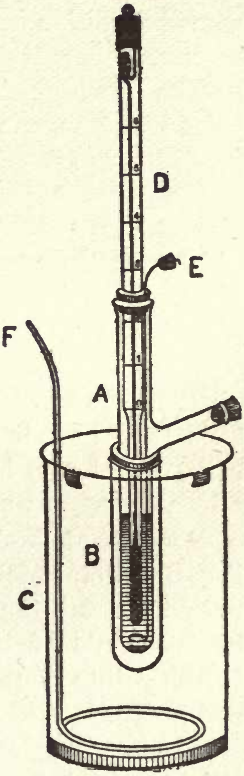

FIG. 4

The freezing-point constant of a solvent is the lowering of its freezing-point in degrees, produced by dissolving in 1000 grams of the solvent in question a gram-molecular weight[1] of a completely unpolymerized, undissociated and unhydrated substance. The necessity of this last-named condition will appear in the last two chapters of this book.

The freezing-point constant of a solvent, like its boiling-point constant, can be calculated from the equation,

$$C = \frac{2T^2}{100L}$$

which was deduced by Van't Hoff[2] and tested by experiment. T is the absolute temperature at which the solvent freezes, and L the heat of fusion of one gram of the solvent.

When this equation is used to calculate the boiling-point constant of a solvent, we must simply reinterpret the symbols. T is then the absolute temperature at which the solvent boils, and L the heat of vaporization of one gram of the solvent.

Results of Molecular Weight Determinations by the Freezing-Point Method. — We have seen that the molecular weights of substances in general in most solvents, at the boiling-points of the solvents, are the simplest possible. It was pointed out that there are many exceptions to this conclusion.

The same general conclusion applies to the molecular weights of substances in solvents at their freezing-points — they are in the simplest molecular condition. Here again exceptions present themselves. A much larger number of solvents can be studied by the boiling-point than by the freezing-point method. More solvents boil between room temperature and, say, 200° than freeze near ordinary room temperature. Nevertheless, a fairly large number of liquids do freeze at temperatures which can be measured with reasonable accuracy. Therefore, the above conclusion is based upon a fair amount of data.

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[1] Gram-molecular weight is the weight in grams equal to the molecular weight.

[2] Any one interested in the deduction of this equation can find it in the *Zeitschrift für physikalische Chemie*, **1**, 497 (1887), or somewhat elaborated in the Author's *Elements of Physical Chemistry*, 4th edition, p. 254 (The Macmillan Co.).

Substances in solution, then, both at the freezing and boiling-points of liquid solvents, are in general, in the simplest molecular condition, *i.e.*, in the same condition as in the gaseous or vapor state. As has been pointed out, this probably has much to do with the relations between solutions and gases discovered by Van't Hoff, and discussed in Chapter V of this book.

Electrolytic Dissociation Measured by the Freezing-Point Method. — We saw when studying the boiling-point method that its most important application was to the problem of electrolytic dissociation. This is also the case with the freezing-point method, especially when historically considered. About twenty-five years ago, when the freezing-point method was first applied to the problem of measuring electrolytic dissociation, there were only two other methods known for dealing with this problem. One of these was based on the power of solutions to conduct the electric current — the so-called conductivity method — and with this we shall become familiar a little later; and the other was based upon certain relations which were worked out in connection with saturated solutions,[1] and which it would lead us too far to discuss here.

The point in the present connection is, that these two methods did not give concordant results and this was used, and with entire justice, by the opponents of the dissociation theory as an argument against that theory — there was no reliable method known of measuring electrolytic dissociation, even if it existed.

In 1892 Ostwald started the author at the task of so improving the freezing-point method of Beckmann that it could be used to measure electrolytic dissociation, to see whether the results obtained by this method would agree with those obtained by either of the other two methods, and if so, with which one.

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[1] *Zeit. phys. Chem.*, **4**, 372 (1889).

Improved Freezing-Point Method. — The first step was to secure a far more sensitive and accurate thermometer than had been used by Beckmann. Ostwald had Goetze construct a thermometer which was ten times more sensitive than any that had ever been made before that time. The thermometer, which was of the Beckmann type, contained in the bulb about 200 grams of mercury, and the capillary was very fine. The entire scale covered a range of only 0.6° and was divided into hundredths and thousandths of a degree. With a telescope it was a very simple matter to read to a ten-thousandth of a degree.

The next part of the problem was so to enlarge the vessel which was to hold the solution that it would contain a large volume of the solution. The vessel selected held just a liter of the solution.

A very efficient stirrer was designed which would keep the liquid well stirred.

This apparatus was found to be very satisfactory when applied to the problem in hand.[1]

Results of Measurements of Dissociation by the Freezing-Point Method. — The dissociations of a fairly large number of salts, over as wide a range of dilution as was possible, was worked out by Jones in the laboratory of Ostwald. It was soon seen that there is, in general, a close agreement between the values found by the freezing-point method and those obtained from conductivity measurements. This can be readily seen from the following table of data. In this table the data from freezing-point lowerings are not taken from the measurements made by Jones in 1892–1893; but from subsequent work done by Pearce[2] in this laboratory in 1907.

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[1] *Zeit. phys. Chem.*, **11**, 110, 529 (1893); **12**, 639 (1893).

[2] *Amer. Chem. Journ.*, **38**, 683 (1907).

Salt	Conc normal	Dissociation from freezing-point lowering	Dissociation from conductivity
$CaCl_2$	0.10	76.35	74.35
	0.05	80.96	80.62
	0.01	90.61	89.67
$SrCl_2$	0.10	81.46	74.17
	0.05	82.65	78.08
	0.01	91.87	89.37
$MgCl_2$	0.10	87.68	73.61
	0.05	90.97	79.78
	0.01	97.10	90.90
$Ca(NO_3)_2$	0.025	90.10	81.13
	0.05	79.27	76.00
	0.25	72.83	61.28
$Sr(NO_3)_2$	0.025	90.27	80.36
	0.05	79.16	74.92
	0.10	73.32	68.59
$Mg(NO_3)_2$	0.02	94.90	85.12
	0.05	84.24	78.80
	0.10	81.95	74.78

These results suffice to show that dissociation as measured by freezing-point lowering, is usually a little larger than as measured by the power of the solutions to conduct the electric current. The meaning of this will be discussed later.

The point, however, which it is desired to bring out by means of the above results, is the *general agreement* between the two sets of results obtained by the above two methods. An examination of the table will show that this is unmistakable.

Since dissociation measured by freezing-point lowering agrees in general with the results obtained by means of the conductivity method, the former, from what was stated earlier, must differ from the values obtained by the solubility method. We had then three methods of measuring dissociation, — conductivity, freezing-point lowering and solubility. The first two gave concordant results, and the third results which differed from those determined by the other two methods. This condition was obviously still far from satisfactory.

Since, however, two methods gave concordant results it seemed probable that there must be some error in the results obtained by the third method. This method was re-examined from the theoretical side, and some of the solubility experiments repeated, with the result that it was found that in applying the solubility method to the measurement of dissociation an assumption had been made which was erroneous; and when this error was corrected, the solubility method gave dissociation values which agreed very satisfactorily with those obtained by both the conductivity and the freezing-point methods.

This point which had given so much trouble was thus satisfactorily cleared up; all three methods of measuring dissociation giving concordant results.

The Three Fundamental Properties of Solutions. — We have seen that the lowering of the vapor-tension of solvents by dissolved substances obeys the law of Raoult. This means that lowering of vapor-tension is one of those properties which depends upon numbers and numbers only, independent of the nature of the dissolved substance and independent of the nature of the solvent.

We have also seen that osmotic pressure is another of these numerical properties. Further, Arrhenius deduced the relation between the lowering of vapor-tension and osmotic pressure.

The lowering of freezing-point, obeying the law of Raoult, is also a property which depends for its magnitude only on the relation between the number of molecules of the solvent and of the dissolved substance — it is an arithmetical property.

The relation between freezing-point lowering and osmotic pressure of solutions has been worked out by Van't Hoff.[1] Indeed, he has deduced the equation for calculating the freezing- and boiling-point constants of a solvent, by combining equations for its osmotic pressure and for the lowering of the freezing-point.

Thus, all three of these fundamental properties of solutions have been connected mathematically; and *these*

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[1] *Zeit. phys. Chem.*, **1**, 496, 497 (1887).

are the three fundamental properties of all true solutions. Given a system which to all external appearances is a true solution, we shall see that it may or may not be a true solution. How are we to determine?

It is only necessary to see whether it has an osmotic pressure which obeys the laws of gas-pressure; whether its lowering of vapor-tension and its freezing-point lowering conform to the laws of Raoult. If such is the case, it is a true solution. If not, it is a colloidal solution, a colloidal suspension or a mechanical suspension, all of which will be discussed later.

While dealing with these numerical properties it should be pointed out that they are the *most important properties,* just because they do depend on numbers and numbers only. It is the study of such properties which yields results of general value.

Whenever we find a property which changes with every change in the composition of the substance, and changes with every change in its constitution, the study of such a property can, at best, lead only to empirical relations; and empirical relations usually disappear as soon as enough facts bearing upon them are brought to light.

These numerical properties may be called *the fundamental properties,* and it is the investigation of these constant properties which really advances the science.

Freezing of Saturated Solutions. — Before leaving the subject of freezing-point lowering, reference must be made to a condition which exists in certain solutions at their freezing-point. When an ordinary solution is frozen the pure solvent separates in the solid phase. If the solution is just saturated at its freezing-point, what will separate when the solution freezes? Obviously, the solid which separates will be a mixture of the solid phase of the solvent and of the solute, *having the same composition as the solution itself.* This mixture, having a definite composition, will continue to separate as long as the solution saturated at its freezing-point is made to freeze by keeping it in the freezing-mixture. Since the solid which separates has a constant composition, the question which would naturally suggest itself is, is this simply a mixture, or is it a chemical compound? Constant composition is a criterion of chemical union, and it was earlier supposed that it was not only a necessary, but a sufficient, condition in determining whether any given system is, or is not, a chemical compound.

These systems, formed by freezing solutions which are just saturated at their freezing-points, Guthrie[1] called *cryohydrates*, "cryo-" from the fact that they are formed at the freezing temperatures, and "hydrates" because in the case of aqueous solutions they contain water, even if in the solid state.

From their constant composition Guthrie supposed these substances to be definite chemical compounds.

Offer[2] proved this not to be the case, and in the following manner. If these cryohydrates are chemical compounds, then, when they are formed, there must be a thermal change, heat being either evolved or absorbed, as in all chemical reactions. Offer found that the amount of heat required to melt a cryohydrate, was just equal to the amount of heat required to melt the ice in the cryhoydrate and dissolve the salt contained in it; thus showing that there was no heat either evolved or absorbed when the cryohydrate was formed, and therefore cryohydrates are *not* chemical compounds.

This same conclusion was confirmed by the following fact. Ice dissolves in alcohol when the whole system is kept below *zero*. Take a cryohydrate which contains a salt insoluble in alcohol, and treat it with alcohol. The ice will dissolve and leave the solid salt behind, showing that they were not in a state of chemical combination, but were simply a mechanical mixture containing the two constituents in a certain definite proportion.

It is very fortunate for chemistry that cryohydrates are not chemical compounds. If they were, the total number of chemical compounds would be greatly increased. Every solution of every substance in every solvent, just saturated at the freezing-point of the solution, when frozen, would yield a cryohydrate, and chemistry would thus be burdened with a still larger number of facts.

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[1] *Phil. Mag.* [4], **49**, **1** (1875); [5], **1**, 49 and **2**, 211 (1876).

[2] *Ber. Wien. Akad.*, **81**, II, 1058 (1880).

The reason that chemistry as a science has developed more slowly than physics is due in part to the nature of chemical phenomena. They obey the law of multiple proportions, which is to say, that chemical combination takes place in steps — 1 of A to 1 of B; 1 of A to 2 of B; 2 of A to 1 of B; and so on. Such phenomena cannot be expressed in *continuous curves*, and we cannot deal mathematically with discontinuous, as we can with continuous phenomena. This condition has held back the application of mathematics to chemistry, and has kept it longer in the condition of an empirical branch of science. The transformation of chemistry from empiricism to an exact branch of science was rendered more difficult also by the large number of chemical facts that were on record. The large number of compounds and the large number of facts, at that time chiefly disconnected and meaningless, which were known about them, made it extremely difficult to discover the fundamental laws underlying these phenomena, and to which they conform.

Were the number of such facts to be indefinitely increased by showing that cryohydrates are definite chemical compounds, it would be an unfortunate day for chemistry.

Some of the fundamental generalizations which have transformed chemistry, in part at least, from empiricism through system into science, have already been considered. The most important of these are the relations between solutions and gases pointed out by Van't Hoff, and the theory of electrolytic dissociation of Arrhenius. To these should be added the law of mass action discovered and mathematically formulated by Guldberg and Waage, and Faraday's law as the basis of valence, which will be discussed later.

It should be noted that these advances have *all* been made by the application of physical and mathematical methods to the problems of chemistry.

CHAPTER IX

AQUEOUS SOLUTIONS OF ACIDS, BASES, AND SALTS — ELECTROLYTES

THREE of the most important classes of chemical compounds are *acids*, *bases*, and *salts*. These three classes taken together constitute the large group known as *electrolytes*. All of these compounds when brought into the presence of water or other dissociating solvents are broken down to a greater or less extent into ions, are electrolytically dissociated. What are the ions of acids and bases?

What is an Acid? — An acid is any compound which in the presence of a dissociating solvent yields hydrogen ions. Every compound which dissociates thus is an acid, and any compound which does not thus dissociate is not an acid.

Some of the consequences of this definition are interesting. No pure, homogeneous substance is appreciably dissociated at ordinary temperatures. Therefore, no pure, homogeneous substance, in terms of this definition, could be an acid, at least of any appreciable strength. Is this conclusion in keeping with the facts? It is. As we have seen, it has been shown that pure, dry hydrochloric acid, even when liquefied, does not decompose carbonates. Pure, dry, hydrochloric acid gas, when dissolved in a nondissociating solvent such as chloroform or benzene, does not decompose carbonates, and does not even color blue litmus red.

Sulphuric acid, when properly dried, does not color blue litmus red, and there are many other examples illustrating the same point. All of these examples tend to confirm the definition of an acid given above.

The older definitions of an acid as a compound which would neutralize a base, and then, of a base as a compound which would neutralize an acid, could scarcely be regarded as definitions in the accepted use of that term.

Logically more correct, but from the standpoint of fact entirely unreliable, is the definition of an acid as a compound whose hydrogen could be replaced directly by metals. When ammonia gas is passed over metallic sodium, one hydrogen of the ammonia is replaced directly by the sodium, sodamide being formed and hydrogen liberated in the sense of the following equation,

$$NH_3 + Na = NaNH_2 + H,$$

and, notwithstanding some work which would indicate acid properties in aqueous solutions of ammonia, we would hesitate to speak of dry ammonia gas as an acid.

All of these older definitions of an acid are entirely inadequate, in that they take into account what an acid usually does, and not at all what it is.

What is a Base? — We define a base as a compound which, in the presence of a dissociating solvent, yields hydroxyl ions.

In terms of these definitions an acid would be represented in general by the equation,

$$RH = \overset{-}{R} + \overset{+}{H}$$

in which $\overset{-}{R}$ may be any atom or group of atoms, usually a group. The general equation for a base would be

$$R_1OH = \overset{+}{R_1} + \overset{-}{OH}$$

in which R_1 may be any atom or group, but is usually a metal atom.

Action of Acids on Bases. — What takes place when we bring an acid in contact with a base? It has long been known that the one *neutralizes* the other. Each destroys the characteristic properties of the other. How?

Whenever an acid acts on a base water is formed. We can see at once how this would take place, if we examine the above equations for acids in general and for bases in general,

$$\overset{-}{\mathrm{R}} + \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{OH}} + \overset{+}{\mathrm{R}}_1 = \mathrm{H_2O} + \overset{-}{\mathrm{R}} + \overset{+}{\mathrm{R}}_1$$

The anion of the acid $\overset{-}{\mathrm{R}}$, and the cation of the base $\overset{+}{\mathrm{R}}_1$, remain after neutralization in exactly the same condition as before, *i.e.*, they remain in the solution in the ionic state, uncombined with one another. The hydrogen ion of the acid and the hydroxyl ion of the base combine and form a molecule of water, and this is what takes place and all that takes place in the process of neutralization. Such are the conclusions from the dissociation theory. Are they true? It is easy to show that if we are dealing with dilute solutions there is no salt formed. The anion of the acid and the cation of the base remain separate, in a word, the salt which would be formed if these ions combined, is not formed at all, but is completely dissociated. To prove this, it is only necessary to measure the dissociation of the solution by any of the well-recognized methods. It is well known, of course, that if such a solution is evaporated, and the water which holds the ions apart removed, they will combine and form a salt. This, of course, has nothing to do with their condition in dilute solution.

To test the second point, whether the hydrogen and hydroxyl ions do combine and form water, is not so simple. The water formed in the process of neutralization would be in the presence of a much larger quantity of water, and would be difficult to detect. The question raised here is really a fundamental one for chemistry. Do hydrogen and hydroxyl ions, in general, when brought into the presence of one another combine, or do they remain separate?

Some light can be thrown on this question in the following way. If hydrogen and hydroxyl ions combine, water is formed and the question resolves itself into this, is pure water dissociated? This question has been answered by determining the conductivity of pure water, and it has been found that pure water is only very slightly dissociated.

Indeed, its dissociation is so slight that, under ordinary conditions, it is negligible. This fact, as far as it goes, answers the question thus: hydrogen and hydroxyl ions cannot remain in the presence of one another to any appreciable extent, uncombined. There are six or eight other independent lines of evidence bearing on this same point; and they all lead to the same conclusion, that hydrogen ions combine with hydroxyl whenever the two are brought together. It would lead us too far to take these up here in any detail.

Importance of This Fact for Chemistry. — The importance of the above fact for chemistry it is difficult to overestimate. Take first the reaction just discussed. If hydrogen ions did not combine with hydroxyl ions, then an acid would not neutralize a base. In the formation of a salt the neutralization of an acid by a base is the first step. It is a necessary, but not a sufficient condition. To get the salt we must concentrate the solution to let the ions of the salt which are present combine. The first step in salt formation from acids and bases, however, is the union of the hydrogen ion of the acid with the hydroxyl ion of the base; and we all know the importance of salts for chemistry.

Indeed, if we glance over chemical reactions in general, we may be surprised to find in how many of them water is formed; and it is usually formed from the hydrogen of one substance combining with the hydroxyl of the other. It is this very union of hydrogen with hydroxyl which often causes the reaction in question to take place. It is not too much to state that a large percentage of all the reactions known to the chemist, owe their existence to the fact that hydrogen and hydroxyl ions cannot remain uncombined in appreciable quantity in the presence of one another.

Heat Evolved When Acids and Bases React. — The dissociation theory applied to the neutralization of acids by bases says, that all that takes place is the union of the hydrogen ion of the acid with the hydroxyl ion of the base, forming water. This can readily be tested in the following way.

If the above conclusion is correct, then every process of neutralization is just like every other process. Neutralization is one and the same act, regardless of the nature of the acid and regardless of the nature of the base — consisting simply in the formation of a molecule of water. If this is true, what quantities of heat are set free when we neutralize equivalent quantities of different acids with different bases? The conclusion is obvious. The heat set free by the neutralization of equivalent quantities of dilute solutions of strong acids with strong bases, *must be constant.* The solutions must be dilute, and the acids and bases both strong in order that the dissociation may be complete.

This conclusion would seem to ask a good deal of any theory. That dilute solutions of all strong acids and all strong bases should, when brought together, liberate exactly the same amount of heat seemed highly improbable until it was tested experimentally. What are the facts?[1]

	Heat
Nitric acid + sodium hydroxide	13,680 cal.[2]
Chloric acid + sodium hydroxide	13,760 "
Hydrochloric acid + sodium hydroxide	13,740 "
Formic acid + sodium hydroxide	13,400 "

When the base is kept constant and the acid varied, the heat of neutralization is a constant to within the limit of error of thermochemical methods.

Let us now take the next step, keep the acid constant and vary the nature of the base brought in contact with it.

Sodium hydroxide and hydrochloric acid	13,740 cal.
Calcium hydroxide and hydrochloric acid	13,950 "
Strontium hydroxide and hydrochloric acid	13,800 "

These results suffice to show that we can vary the acid or vary the base as we like, provided we keep within the category of strong acids and strong bases; the heat of neutralization is a constant. This constant is about 13,700 calories, which is of course the heat of combination of the hydrogen with the hydroxyl ions. The conclusion from the dissociation theory is thus completely substantiated by the experimental facts.

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[1] Ostwald: *Lehrb. d. allg. Chem.*, vol. 2, I.

[2] A "calorie" is the amount of heat required to raise the temperature of one gram of water one degree centigrade.

Exceptions Presented by Weak Acids and Weak Bases. — It was stated above that the law of the constant heat of neutralization holds only for strong acids and strong bases. The reason for this is almost obvious. If the acid is weak it would not be completely dissociated in the solution. If the base is weak it also would not be completely dissociated. If the solutions of acid and base brought together are not completely dissociated, as the dissociated portions neutralize one another the undissociated portions will dissociate. But the dissociation of molecules into ions has a thermal value, — heat is either liberated or absorbed. When such incompletely dissociated solutions are brought together, we have set free not only the heat of neutralization, which, as we have seen, is the heat of combination of hydrogen and hydroxyl ions, but in addition the heat of ionization which may be either a positive or a negative quantity.

When weak acids are brought in contact with weak bases, we should therefore expect not a constant heat of neutralization, but a value which might be either greater or less than the thermal constant for strong acids and strong bases, and which would vary somewhat for every weak acid and for every weak base.

The facts are:

Acetic acid and ammonium hydroxide	11.900 cal.
Acetic acid and barium hydroxide	13.400 "
Propionic acid and barium hydroxide	13.400 "
Valeric acid and sodium hydroxide	14.000 "

Here again, the conclusion from the theory of electrolytic dissociation is fully confirmed by the facts of experiment.

Theory of Electrolytic Dissociation as a Correlator of Facts. — The above relations suggest another use of a law or generalization such as the theory of electrolytic dissociation. Before this theory told us what was meant by neutralization, we had as many separate problems of neutralization to deal with as we had individual acids and individual bases. Every act of neutralization was different from every other act, because a different salt was formed whenever we varied the acid and whenever we varied the base.

Now such is not the case. All acts of neutralization are one act. What takes place in every case, and all that takes place if the solutions are dilute, is the formation of a molecule of water. No salt is formed unless the solutions containing the ions which would form the salt is evaporated or otherwise concentrated.

Thus, all processes of neutralization, and there are as many as there are acids and bases, become *one process*, and the whole problem of neutralization becomes *one problem*, which immensely simplifies the whole subject.

This coordination and correlation of heterogeneous and often chaotic and meaningless facts is one of the most important functions of a generalization or law. A law, then, tends not only to convert empiricism and system into science, but also, by correlation, to simplify greatly the branch of science to which it applies.

Thermoneutrality of Solutions of Salts. — While discussing the thermal changes that take place in solution, one other property of solutions should be mentioned in this connection. Very dilute solutions of neutral salts when mixed show no thermal change. This fact, when first discovered, was very perplexing. Every chemical change, it was said, was accompanied by a thermal change. The fact is correct, but we shall see that the statement of it was faulty, in that it confused cause and effect. Here was certainly a chemical act and yet no thermal change, — a chemical act, because if we mix solutions of two salts, say calcium chloride and sodium nitrate, and evaporate the mixture to dryness we obtain four salts — calcium chloride, calcium nitrate, sodium chloride and sodium nitrate. If we start with two salts and end with four, there must have been a chemical act somewhere in the process.

This relation was discovered long before we had the theory of electrolytic dissociation to explain it. The explanation now is not only simple, but this law is a necessary consequence of the theory of electrolytic dissociation. Calcium chloride in solution is dissociated thus,

$$CaCl_2 = \overset{++}{Ca}, \overset{-}{Cl}, \overset{-}{Cl}$$

sodium nitrate in solution thus,

$$NaNO_3 = \overset{+}{Na}, \overset{-}{NO_3}$$

When we mix dilute solutions of these two salts, the ions of both remain in the mixture in exactly the same condition of freedom as in the separate solutions. There is no combination — no salt is formed, no chemical act takes place, and there should be no thermal change.

When the solution is evaporated and the water which held the ions apart removed, they combine in all possible ways and form the four salts. This, however, has nothing to do with what takes place on simply mixing the dilute solutions of the two salts. Thus, the law of the thermoneutrality of salts presents no further difficulties, now that we have the theory of electrolytic dissociation.

Importance of Energy Changes for Chemistry. — We have just discussed the energy change which takes place when acids are neutralized by bases, and have pointed out that every chemical reaction is always accompanied by a thermal change, as was stated. This raises the question, of what significance are the energy changes for chemistry?

When the law of the conservation of energy was discovered, it was supposed to be simply a law of physics, and chemists paid comparatively little attention to it. This was due primarily to the fact that chemists of that period did not pay very serious attention to physics in general, being more interested in the preparation of compounds, and in the working out of their composition and constitution, than in discovering the physical principles that underlie chemical science. This was perfectly natural when we consider the development of chemistry at the time to which we are referring. It was not until the great French chemist, Berthelot, pointed out the importance of energy changes for chemistry, and made his famous thermochemical measurements from which he deduced fundamental laws, that chemists began to see the significance of changes in energy for the whole science of chemistry.

Since the time of Berthelot's thermochemical work,[1] we have recognized that the cause of all chemical reaction is to be found in the different amounts and potentials of intrinsic energy in the substances brought together. When this difference is sufficiently great, some of the intrinsic energy is converted into heat, light, or electricity — always some into heat, and the substances rearrange themselves in new combinations which are more stable under the new conditions. A chemical reaction is, then, not "accompanied" by a thermal change, but is *caused* by it. We could more truly say that the thermal change is "accompanied" by the chemical reaction.

As soon as the importance of energy changes for chemistry was pointed out, chemists began to realize that the law of the conservation of energy is as important for chemistry as it is for physics. The two laws, the law of the conservation of mass and the law of the conservation of energy, lie right at the foundation of chemical science; chemistry being quite as much dependent for its existence upon energy changes as is physics.

Color of Dissolved Substances. — Many solutions in water are colorless, and others are colored. Why this difference? Light is a series of vibrations of different wave lengths in the hypothetical ether. White light contains a large number of such vibrations. When all of the ether vibrations pass on through the solution, it is white or colorless as we say. When all of these vibrations are cut off or stopped, the solution is opaque or black. When some of the vibrations are cut off and others allowed to pass on through, the solution is colored; the color depending upon the particular wave-lengths of the vibrations that are transmitted. If the shorter wave-lengths are stopped, the solution has the color of the longer wave-lengths which pass on through. If the longer wave-lengths are cut out, the solution has the color of the shorter wave lengths that are transmitted.

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[1] *Essai de Méchanique Chimique.*

The solution may cut out some of the longer and some of the shorter wave-lengths, in which case the solution would have the color of the transmitted light, whatever it is. It is thus obvious that solutions may have any color.

Absorption of Light due to Resonance. — The question arises, what is meant by absorption of light? To use the prevailing theory, how can vibrations in the ether be absorbed or stopped?

If the ether vibrations find something in the solution which they can set vibrating with the same period as their own — can throw into resonance with themselves — their energy is expended in setting this something vibrating, and the original vibration is stopped. Those vibrations in the ether which do not find in the solution anything which they can set vibrating with their own period, are not stopped, but pass on through. Resonance produces opacity; the lack of resonance, transparency.

Color in Solution May be Ionic or May be Molecular. — The color of solutions acquired a new interest after the theory of electrolytic dissociation was proposed. If dilute solutions of electrolytes contain only ions, then all the properties of such solutions, including their color, must be due to the ions. This could readily be tested, and it was done by Ostwald[1] in the following manner.

Select a series of salts of an acid with a colored anion, say fluorescein, the salts having colorless cations; and see whether the solutions of these different salts all have the same color. This, of course, could not be tested by the eye, since the eye as a measure of color is most deceptive. A spectroscope must be used for this purpose, and Ostwald used a prism.

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[1] *Zeit. phys. Chem.*, **9**, 579 (1892).

The absorption bands for the different solutions were photographed the one above the other. These bands correspond to the wave-lengths of light that were cut out or absorbed by the solutions.

Take for example the salts of fluorescein.[1] The ammonium, cobalt, magnesium, cadmium, barium, manganese, lithium, nickel, potassium, and zinc salts were studied.

Salts of Fluorescein

	λ = Å.U.
Ammonium	2866
Cobalt	2867
Magnesium	2865
Cadmium	2866
Barium	2866
Manganese	2867
Lithium	2865
Nickel	2866
Potassium	2866
Zinc	2866

The absorption bands for all of these salts of fluorescein coincide almost to within the limit of experimental error. Ostwald carried out similar measurements with salts of eosin, iodoeosin, and other acids with colored anions, the salts chosen having colorless cations. Similar results were obtained in every case; the absorption of the different salts of any one acid being the same to within the limit of experimental error.

Having studied the salts of acids with colored anions, the cations being colorless, Ostwald turned to salts of bases with colored cations, the anions being colorless. Thus, he studied the *p*-rosaniline salts and aniline violet salts of twenty acids with colorless anions. He photographed the results for each base, the one above the other, and found that the absorption lines coincided to within experimental error. A few of his results for aniline violet with a number of acids are given in the table on the opposite page.[2]

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[1] *Zeit. phys. Chem.*, **9**, 587 (1892).

[2] *Ibid.*, 599.

Salts of Aniline Violet

	λ = Å.U.
Acetate	2534
Benzoate	2534
Hydrochloride	2533
Nitrate	2534
Butyrate	2533
Trichloracetate	2533
Glycolate	2534
Lactate	2533

These results obtained by Ostwald fall right in line with the dissociation theory for electrolytes. The colors of these substances are the colors of the ions.

We know, however, that molecules also can have color. Many solutions of non-electrolytes which are completely undissociated are colored. Again, many substances in the pure, dry condition are colored, and these are, of course, undissociated.

In the present connection it should be pointed out that the crystals of many substances which crystallize with water are colored, and the crystals have approximately the same color as their aqueous solutions. What is the explanation? The *molecules are dissociated in their water of crystallization,* and the ions thus formed show their characteristic color.

Cause of Color in Solution. — We have seen that color is due to resonance. Those wave-lengths of light which can find something in the solution which they can throw into resonance, are cut out or absorbed, the remaining vibrations passing through and giving the characteristic color to the solution. This raises the question, what is it in solution that is thrown into resonance by the light? Is it the molecule, the ion, the atom, or the electron or electrical charge[1] of which all the atoms are made?

We shall see in the last chapters of this book that work in this laboratory has made it almost certain that absorption in solution is not due directly to the molecules, nor to the atoms, and not even to the ions, but is due to the electrons.

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[1] See Author's *Electrical Nature of Matter and Radioactivity,* 3d edition (The Van Nostrand Co.).

It is interesting to note that this was predicted by Ostwald long before Thomson had done his epoch-making work on the electron. Ostwald pointed out the importance of the electrical charge on the ion as conditioning its color, and this electrical charge we now know is nothing but the electron of Thomson.

Take as an illustration of this point the well-known salts, potassium ferrocyanide, $K_4Fe(CN)_6$, and potassium ferricyanide, $K_3Fe(CN)_6$. Ostwald supposed that these compounds dissociated as follows:

$$K_4\,Fe(CN)_6 = \overset{+}{K},\overset{+}{K},\overset{+}{K},\overset{+}{K},\ \overset{\underline{\equiv}}{Fe}(CN)_6$$

and

$$K_3\,Fe(CN)_6 = \overset{+}{K},\overset{+}{K},\overset{+}{K},\ \overset{\equiv}{Fe}(CN)_6$$

The color of the ferrocyanide is yellow; while the color of the ferricyanide is greenish; and the latter has *many times* the coloring power of the former. Why this difference?

The color of both solutions is due to the ferrocyanogen ions since the potassium ion is colorless. The ferrocyanogen ion from the ferrocyanide has four negative charges upon it, while the ferrocyanogen ion from the ferricyanide has three negative charges upon it. Ostwald would account for the difference in the color as due to this difference in the *number of charges* which these ions carry; and this, as has been stated, is in perfect accord with our own recent work on the absorption spectra of solutions.

Color Changes and Volumetric Analysis — Indicators. — The whole science of volumetric analysis is based upon certain changes in color of certain substances known as indicators. These substances have been used, and these changes in color employed, in volumetric analysis from the early history of this important branch of quantitative chemistry. The indicators were, however, used for a long time largely mechanically. Certain things were done and certain results obtained without knowing just why.

It remained for Ostwald to clear up this subject as he has cleared up so many others. The Ostwald theory of indicators has taken this subject from the rank of pure empiricism and placed it for the first time upon a really scientific basis. Let us see what it is.

The Ostwald theory, of course, is based upon the theory of electrolytic dissociation as a starting point. Indicators are either weak acids or weak bases. Further, the dissociated compound, the ions, must have a *different color* from the undissociated molecules. These are the keys to the whole theory.

Take *phenolphthalein;* its molecules are colorless and its anion colored. Phenolphthalein, being a weak acid, in the presence of a strong acid, or in the presence of water alone, is undissociated. When a strong base is added to phenolphthalein it dissociates, yielding the anion with its characteristic color. This compound illustrates the type of indicator where the molecule is colorless and the anion colored.

Litmus illustrates another type of indicator. Like phenolphthalein, litmus is a weak organic acid; but unlike phenolphthalein the molecules of litmus acid are colored, and are colored red. When a base is added to litmus acid, the molecules are caused to dissociate and set free the anion of the acid which is colored blue — the molecules have one color and the ions another.

Another acid indicator which, however, is a much stronger acid than litmus, is *methyl orange.* The molecules are red, and therefore this indicator in the presence of a strong acid is red. The anions are yellow. Therefore, in the presence of a base this indicator dissociates, liberating the yellow anions.

Exactly the same relation obtains for *methyl red,* which is very closely allied chemically to methyl orange. Here the molecules are red, and the reaction is therefore red in the presence of acids. The anion is yellow, and this indicator therefore reacts yellow in the presence of a base.

Another acid indicator is *corallin,* or rosolic acid. It is a weak organic acid, the molecules being yellow. When a base is added the red anion is set free.

Stieglitz's Views in Reference to Phenolphthalein. — The view of Stieglitz[1] in reference to the action of phenolphthalein as an indicator goes further than the theory of Ostwald. The latter, from what has been said above, simply assumes that the weak, colorless phenolphthalein molecules dissociate into hydrogen ions which combine with the hydroxyl ions of the base, and into an anion which has the color characteristic of this indicator in the presence of bases.

Stieglitz, commenting on the Ostwald theory of indicators says, "It is extremely probable, moreover, that this theory is wrong in so far as the interpretation of the cause of the change of color is concerned." "While most likely wrong in regard to the one question of change of color, Ostwald, in his theory of indicators, has undoubtedly laid down correctly the guiding principles of the proper theoretical treatment of the second, scientifically far more important, question concerning the varying sensitiveness of the indicators to acids and bases."

"In[2] view of what chemists have known for over a quarter of a century about the intimate connection between color production and constitution of organic compounds, the explanation that phenolphthalein without a single chromophoric group should become intensely red by forming the ion without any chromophoric group appeared from the outset as extremely unlikely."

Stieglitz then points out that it had been shown by Bernthsen that when phenolphthalein forms a salt, as when treated with an alkali, there is an internal rearrangement, giving rise to the highly colored quinoid ($:C_6H_4:O$) group, which explains the appearance of the color. "The sodium salt is, no doubt, incidentally ionized in solution, but that this ionization is merely a coincidence and not a cause is established by the fact that the solid, dry, non-ionized silver salt is also intensely colored (violet)." Says Stieglitz, "more recently Hantzsch has shown that, in general, the change of colorless organic compounds into highly colored salts is invariably accompanied by a modification of the constitution affecting a chromophoric group."

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[1] *Journ. Amer. Chem. Soc.*, **25**, 1112 (1903.)

[2] *Ibid.*, 1114.

According to Stieglitz the ionization alone is not the cause of the color, but the ionization and the internal change in constitution take place simultaneously, and it is the latter which is the cause of the color.

In the use of indicators in quantitative analysis it is important to know the degree of dissociation of the weak acids and weak bases used as indicators. The so-called "constants" of indicators are a function of their dissociations. These constants[1] have recently been worked out radiometrically in this laboratory for phenolphthalein, methyl orange, and corallin.

Amphoteric Compounds — Importance in Chemistry. — We have considered acids as dissociating always into a hydrogen cation, and into an anion whose composition depends on the particular acid in question. Wherever we have acid properties we have hydrogen ions, and wherever we have hydrogen ions we have acid properties.

Similarly, bases have been referred to as compounds which, in the presence of a dissociating solvent, yield hydroxyl ions. Basicity and hydroxyl ions always go hand in hand.

It might be inferred from this that a compound which under one set of conditions yields hydrogen ions, under all conditions would dissociate yielding ions of hydrogen; and, similarly, a compound which under one set of conditions would split off hydroxyl ions, would under all conditions yield the hydroxyl ion. Such is not the case. A compound may under some conditions dissociate into hydrogen ions, while under other conditions the same compound may dissociate yielding hydroxyl ions. Such a compound which is capable of dissociating now as an acid, and now as a base, is known as an *amphoteric electrolyte.*

There is a fairly large number of examples of these substances, both in general chemistry, and among the compounds of carbon. We need only mention zinc hydroxide, which in the presence of an acid or hydrogen ions dissociates thus,

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[1] *Journ. Amer. Chem. Soc.,* **37,** 776 and 1694 (1915.)

$$Zn(OH)_2 = \overset{++}{Zn}, \overset{-}{OH}, \overset{-}{OH}$$

while in the presence of a base or hydroxyl ions, it dissociates thus,

$$Zn(OH)_2 = \overset{=}{ZnO_2}, \overset{+}{H}, \overset{+}{H}$$

In the first case zinc hydroxide dissociates as a base; in the second as an acid. As a base it neutralizes acids and forms zinc salts; as an acid it neutralizes bases and forms zincates. It is a well-known fact that zinc hydroxide dissolves in an excess of sodium hydroxide almost as readily as in hydrochloric acid.

Take another example illustrating the same point — lead hydroxide. In the presence of an acid it dissociates as a base, thus,

$$Pb(OH)_2 = \overset{++}{Pb}, \overset{-}{OH}, \overset{-}{OH}$$

In the presence of a base, it dissociates as an acid, thus,

$$Pb(OH)_2 = \overset{=}{PbO_2}, \overset{+}{H}, \overset{+}{H}$$

As a base lead hydroxide reacts with acids forming salts of lead. As an acid it reacts with bases forming plumbates.

There are many other examples of amphoteric substances in general[1] as in organic chemistry, but the above suffice to illustrate the principle.

Amphoterism and Biological Processes. — The number of amphoteric substances among the compounds of carbon is very large indeed. We need only mention asparagine, sarcosine, leucine, tyrocine, and especially the proteids in general; and the rôle of the latter in living processes is very important. They contain both the carboxyl (COOH) and the amino (NH_2) groups, and can therefore dissociate either as acids or as bases. In this connection see L. J. Henderson, "The Fitness of the Environment"; and S. L. Sörensen, Ergebnisse der Physiologie, vol. 12 (1912).

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[1] *Elements of Inorganic Chemistry*, H. C. Jones, 3d edition, p. 389. (The Macmillan Co.)

Hydrolysis at Ordinary and at High Temperatures. — The only action of water on salts that we have thus far discussed is that of electrolytic dissociation. The molecule of the salt is broken down directly by water into a cation or cations charged positively, and into an anion or anions charged negatively. There is another kind of dissociation of salts effected by water which must be discussed here — *hydrolytic dissociation* — which differs fundamentally from electrolytic dissociation, although the products of hydrolytic dissociation are always more or less electrolytically dissociated.

Solutions of certain salts react acid, *e.g.*, aluminium chloride; while solutions of sodium carbonate react alkaline. This fact was known a long while before it could be explained. It was said that the former reacts acid because hydrochloric acid is a stronger acid than aluminium hydroxide is a base. A residue of the acid properties still clings to the salt. Similarly, sodium carbonate reacts alkaline because sodium hydroxide is a stronger base than carbonic acid is an acid.

In the light of what we know today about acids and bases, this, of course, explains nothing, and is hardly more than words.

We now know what is meant by hydrolysis, and why solutions of some salts react acid and others basic. Aluminium chloride, for instance, is acted upon by water, to a slight extent at least,

$$2AlCl_3 + 3H_2O = 6HCl + 2Al(OH)_3$$

Aluminium hydroxide, being a weak base, is only slightly dissociated, and yields only relatively few hydroxyl ions. Hydrochloric acid, on the other hand, is a strong acid and is strongly dissociated into its ions. The hydrogen ions predominate over the hydroxyl, whence the acid reaction of the solution.

In the case of sodium carbonate exactly the opposite is true. The reaction with water is represented thus,

$$Na_2CO_3 + 2H_2O = 2NaOH + H_2CO_3$$

Sodium hydroxide, being a strong base, is largely dissociated and yields a large number of hydroxyl ions. Carbonic acid, being a weak acid, is only slightly dissociated and consequently yields only a few hydrogen ions. The hydroxyl ions predominate in number over the hydrogen ions and give the alkaline reaction to the solution.

The question arises, is hydrolysis a general phenomenon? Are salts in general hydrolytically dissociated by water? The answer is, yes. Salts of strong acids with strong bases, however, undergo such slight hydrolysis that it can usually be disregarded. Salts of weak acids with weak bases are the most strongly hydrolyzed. Salts of weak acids with strong bases, and of weak bases with strong acids are hydrolyzed to some extent, the magnitude of the hydrolysis depending on the actual strengths of the acid and base which formed the salt in question.

It may be said in general that salts of the alkalies with strong acids are so little hydrolyzed by water at ordinary temperatures, that the hydrolysis is negligible. Salts of the alkaline earths, even with the strongest acids, are hydrolyzed to a slight extent, while salts of weaker bases, such as aluminium hydroxide, ferric hydroxide, etc., are, even at ordinary temperatures, very appreciably hydrolyzed.

It will be noted that the products of hydrolytic dissociation are always more or less electrolytically dissociated by water — hydrolytic dissociation is always accompanied by more or less electrolytic dissociation.

Effect of Temperature on Hydrolytic Dissociation. — The effect of rise in temperature on hydrolysis is a matter of interest not only for the chemist, but for the geologist. This problem has been studied by A. A. Noyes[1] and his coworkers. They used a closed bomb to hold the solutions at more elevated temperatures, and calculated the change in hydrolysis with rise in temperature from the change in the conductivity. They worked from 0° up to 306° and at even higher temperatures.

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[1] *Zeit. phys. Chem.*, **46**, 323 (1903.)

We have seen that the most strongly hydrolyzed salts are the salts of weak acids and weak bases. Noyes and his co-workers studied the effect of rise in temperature on the hydrolysis of ammonium acetate — a salt of a weak acid and a weak base. They found that for a rise in temperature from 0° to 306°, the hydrolysis of ammonium acetate increased about three hundred times.

The effect of rise in temperature on the hydrolytic decomposition of salts by water is of geological significance and importance. Well down beneath the surface of the earth highly heated water-vapor comes in contact with the rocks which are also heated to very high temperatures. The decomposition of the silicates and other rocks by water at very high temperatures is now intelligible in the light of the work of Noyes on the rapid increase in hydrolysis with rise in temperature.

CHAPTER X

A FEW ELECTRICAL PROPERTIES OF AQUEOUS SOLUTIONS OF ELECTROLYTES

THE difference between electrolytes and non-electrolytes was clearly pointed out in an earlier chapter. It was shown that electrolytes are those substances whose solutions conduct the current, and that non-electrolytes are those whose solutions do not conduct.

Since solutions of electrolytes conduct electricity, the particles in such solutions must be charged electrically.

The first to study scientifically and successfully electrical conduction in solution was the great experimenter, Michael Faraday. He passed different amounts of electricity through the solution of the same salt, and determined the amounts of the metal deposited upon the cathode. In this way he discovered the first part of his well-known law, or his first law.

Faraday's First Law. — Faraday found that when double the amount of electricity was passed through a solution, exactly double the amount of salt was decomposed and double the amount of metal deposited upon the cathode. He studied the decompositions of a large number of substances, using different amounts of current, and always found that the amount of decomposition was proportional to the amount of the current passed through the solution. He formulated his first law as follows: *The amount of salt decomposed by the electric current is proportional to the amount of electricity passed through the solution.*

This law is of importance in that it gives us a ready means of measuring quantity of electricity. Knowing the amount of decomposition of a salt like silver nitrate effected by passing, say, one coulomb of electricity, it is only necessary to pass the current in question through a solution of silver nitrate and weigh the amount of silver deposited upon the cathode, in order to know how much current was passed through the solution. The silver, copper, and gas voltameter are all based upon this first law of Faraday.

Faraday's Second Law. — Faraday then raised the question, is there any relation between the amounts of the different metals deposited by the same amount of current, and if so, what is this relation?

To test this, Faraday passed the same current through a series of solutions of salts of different metals and collected the metals on the several cathodes and weighed them. He found the following very remarkable relation. The amounts of the different metals thrown out by the same current are proportional to the atomic weights of the metals, provided all the metals in question have the same valence. If they have different valences, Faraday found that the *amounts of the metals thrown out by the same quantity of electricity are proportional to the atomic weights of the metals divided by their respective valences;* and this is the second law of Faraday.

Of what significance is this law? What have the valences of the different metals to do with the decomposition of their salts by the electric current? These are questions which the second law of Faraday would naturally suggest. Their answer has told us what chemical valence really means.

Second Law of Faraday and Chemical Valence. — When a given current is passed through solutions of salts of metals having the same valence, as already stated, the amounts of the different metals deposited are proportional to their atomic weights. This means that the same numbers of atoms of all the different metals are deposited by the same amount of electricity. This is the same as to say that *all atoms having the same valence carry exactly the same amount of electricity.*

The law, however, goes farther in its bearing on, and explanation of chemical valence. If the metals have different valences, the amounts deposited are proportional to the atomic weights divided by the several valences. This shows exactly what is the difference between a univalent, a bivalent, a trivalent, and an *n*-valent element. They carry different numbers of unit charges of electricity — the number determining the valence of the ion. A univalent ion carries one unit charge of electricity or one free electron; a bivalent ion two unit charges or two free electrons; a trivalent ion three unit charges or three free electrons; an *n*-valent ion *n* unit charges or *n* electrons.

Chemical valence is thus shown to be connected in some fundamental way with the number of free unit charges of electricity, or electrons, upon the ions. This second law of Faraday simply shows that the one is proportional to the other. It does not answer the question whether the one is the cause of the other. This has, however, been answered; and since the question of chemical valence is so fundamental for all chemistry, the answer will be given here, at the risk of a slight digression from the questions now more directly under discussion.

Nature of Chemical Valence. — There are few subjects upon which more has been written than the subject of valence, and few subjects about which there has accumulated so much unsatisfactory literature. The reason for this is obvious to any one who has read a few of the many papers on this subject.

The attempt has frequently been made to discuss chemical valence without any clean-cut definition of the subject under discussion. The result is just what would be expected. When we start with nothing definite we can hope to lead to nothing definite. It is scarcely hypercritical to state that many of the papers which have been written upon the subject of valence, when carefully analyzed, are little more than words, largely for the reason indicated above.

The second law of Faraday has placed the whole subject of chemical valence upon a definite physical basis, and has shown the proportionality between the valence of an ion and the number of charges which it carries.

It remained for Ostwald to show the causal relation between these two phenomena — that chemical valence is essentially the chemical expression of the number of free electrons upon the ions and their attractive and repellent forces. This was done by the following experiment in which chemical valence was synthesized, if you please, and out of what? Out of electrical energy; and done in such a way that there could be no reasonable question as to the result.

Experiment Demonstrating the Nature of Chemical Valence. — A cell was constructed in the following manner.[1] Into one of two beakers was introduced a solution of ferrous chloride. A solution of potassium chloride was introduced into the second beaker; and into each beaker, a platinum wire serving as an electrode. The two electrodes were attached to a galvanometer. The two beakers were connected by a siphon filled with the solution of potassium chloride. Chlorine gas was conducted into the solution of potassium chloride. When this was done the galvanometer showed a current flowing on the outside of the cell from the electrode surrounded by the potassium chloride into which chlorine gas has been conducted to the electrode surrounded by the neutral ferrous chloride. The ferrous chloride quickly showed the presence of ferric chloride.

The action of this cell is as follows. When chlorine gas is conducted into the solution of potassium chloride the chlorine undergoes ionization, passing over into anions. Whence does it get the negative charges of electricity necessary to convert the chlorine atoms into ions? The only possible source is the platinum electrode immersed in the potassium chloride. This electrode, having given up negative electricity in converting the chlorine atoms into chlorine ions, is consequently charged positively. The positive electricity which thus accumulates upon this electrode, due to the ionization of the chlorine, flows around through the galvanometer to the other electrode immersed in the solution of ferrous chloride. The ferrous chloride is, of course, dissociated by the water into *ferrous ions* each carrying two positive charges of electricity, and into two chlorine ions each carrying one negative charge of electricity. The ferrous ion with its two positive charges can take up one more positive charge yielding a *ferric ion,* which has three positive charges upon it. It does so, getting the third positive charge from the platinum electrode immersed in the solution of the ferrous salt.

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[1] *Zeit. phys. Chem.*, **9**, 550 (1892).

The ferric ion with its three positive charges can pair off against three chlorine ions, each with one negative charge. This is the condition in a solution of ferric chloride. The question is, whence comes the third chlorine ion?

It is well known that all anions move against the current. When the chlorine gas conducted into the solution of potassium chloride becomes ionized, the chlorine ions move against the current through the solution of potassium chloride, and may be regarded as moving through the siphon over to the ferrous chloride and pairing off against the ferrous ions which have been converted into ferric ions by taking positive electricity from the electrode immersed in the solution surrounded by the iron salt.

The fundamental point of this experiment is, that the valence of a bivalent or ferrous ion is raised to a condition of trivalency, or to the ferric condition, by simply adding electricity to it, and doing this under such conditions that we can say with reasonable certainty that *nothing else has taken place.* We have thus created valence, as it were, out of electrical energy.

From this experiment alone we know that valence is but the chemical expression of the number of electrons or free electrical charges upon the ions. Thus valence is placed upon a perfectly rigid physical basis, and can and should be discussed primarily in terms of Faraday's law.

It may be noted in passing that this experiment illustrates also another principle, as was pointed out by Ostwald.

Using the term oxidation in the old sense of increase in valence, the valence of the ferrous ion is raised, or the ferrous ion is oxidized by chlorine which does not come in contact with it.

This experiment may then be regarded as showing that contact is not essential to chemical action; things may react that do not touch one another.

Ostwald[1] has described another experiment illustrating chemical action without mechanical contact, which is much more easily carried out, and more striking in its results than the above.

Electrolytes Conduct Only by Undergoing Electrolysis. — It has long been known that when an electric current is passed through a solution of an electrolyte, the electrolyte undergoes decomposition, the cations moving to the cathode and the anions to the anode. This raises the question as to whether this is the only way in which electricity can pass through a solution of an acid, base, or salt. Might not small amounts of electricity get through solutions in some other way than by being carried by the ions which are simultaneously discharged?

This question was answered once and for all by Ostwald and Nernst[2] in the following way. A large balloon flask was covered with tin foil, which was connected with the condenser of a Holtz machine and charged positively. The flask was filled with dilute sulphuric acid, which was connected by means of a siphon with sulphuric acid in a dish. Into the sulphuric acid in the dish was inverted a glass tube drawn out to a fine capillary below and partly filled with mercury. The mercury and the sulphuric acid came in contact in the capillary tube. The mercury in this tube was connected with the earth. When the frictional machine was set in operation, the tin foil around the flask became charged positively. This attracted electrostatically the $\overset{=}{SO_4}$ ions within the flask coming from the sulphuric acid, and repelled the hydrogen ions from the same acid.

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[1] *Zeit. phys. Chem.*, **9**, 540 (1892).

[2] *Ibid.*, **3**, 120 (1889).

The hydrogen ions coming in contact with the mercury in the capillary tube gave up their charges to the mercury and separated as hydrogen gas. This could be seen in the fine capillary by means of a microscope. If the capillary was carefully calibrated, the amount of hydrogen which separated could be accurately measured. Ostwald and Nernst showed that when 0.000005 of a coulomb of electricity was passed through the solution of sulphuric acid, hydrogen gas was separated. They showed that Faraday's law holds to within this limit.

Another experiment devised by Ostwald, bearing on this same point, although only theoretical, should be referred to on account of its historical interest.

Take two beakers, and partly fill them with a solution of potassium chloride. Connect the two with a siphon filled with the solution of potassium chloride, and bring up to one beaker a condenser charged, we will say, negatively. This will attract electrostatically the positively charged potassium ions, and repel the negatively charged chlorine ions. Now remove the siphon, when the beaker next to the condenser will contain an excess of the positively charged potassium ions. Connect the contents of this beaker with the ground, and the excess of potassium ions will lose their charges to the earth and remain as uncharged potassium atoms. These would then react with water in the usual way and liberate hydrogen gas.

Ostwald stated that some one wrote him that he tried this experiment, and failed to observe the hydrogen. Ostwald then calculated the size of condenser that it would be necessary to use to liberate enough hydrogen to be seen escaping from the solution of potassium chloride, taking into account the solubility of hydrogen gas in water. The condenser if in the form of a cube would have an edge a kilometer long, in a word, the condenser would be a cube whose edge would be about three-fifths of a mile.

The reason for all this will become obvious when we consider the enormous amount of electricity carried by a few ions. A very large amount of electricity is necessary to cause enough ions to separate to be visible to the naked eye. That is the reason why the above described experiment of Ostwald and Nernst was devised to prove especially to Du Bois Raymond the correctness of the theory of electrolytic dissociation of which the result obtained is a necessary consequence.

The Laws of Faraday Apparently Rigid Laws of Nature. — It will be recognized at once that the first law of Faraday is a fundamental law of electrolytic conduction. Upon its rigidity depends our knowledge of the passage of electricity through solutions of electrolytes. Such a fundamental law would naturally be very exhaustively tested. The strength of the current employed to effect the electrolysis would be greatly varied. The temperature would be changed, and also the strength of the solution through which the current was passed. All of these variables have been studied and Faraday's law has stood the test as a rigid law of nature would do.

The rigidity of Faraday's law under all conditions has been called in question, and in the following way. A solution electrolyzed under high pressure separated *less of the electrolyte* for a given amount of current, than when electrolyzed under ordinary pressure. This could be interpreted as showing that under these conditions Faraday's law did not hold.

Pressure was brought to bear on the solution by compressing the gas above the solution. Under these conditions more gas would, from Henry's law, dissolve than when the gas was under only normal pressure. It was shown that a small part of this dissolved gas was ionized and this assisted in carrying the current through the solution. When this was taken into account it was found that the law of Faraday held also under this condition.

The Laws of Faraday are to be placed among the few rigid laws of nature to which no exception is thus far known, and the number of such laws is very few indeed.

The Nature of Electrolysis. — When a continuous current is passed through a dilute solution of an acid, base, or salt, hydrogen is liberated at the cathode and oxygen at the anode. If we are dealing with the salt of a metal which does not act on water the metal itself is deposited at the cathode. As we have seen, the only way an electric current can pass through a solution or through water is by electrolyzing the dissolved substance or the solvent. Such are some of the facts of electrolysis. What is their explanation?

We have become familiar with the theories proposed by Grotthuss and by Clausius to account for the phenomena of electrolysis. The theory of the electrolysis of acids, bases, and salts, which was held for forty years, was based upon the suggestions made by Clausius. The theory, as it was applied, is as follows.

Older Theory. — When the current is passed through a solution of an *acid*, the hydrogen ions of the acid move over to the cathode, give up their positive charges, and escape as hydrogen gas. The anion moves over to the anode, gives up its charge, but not being volatile does not escape. It "acts on water," as it was said, liberating oxygen and combining with the hydrogen, reforming the acid.

The electrolysis of a *base* was strictly analogous. The hydroxyl anions move over to the anode, give up their charges, two of them react with one another, forming a molecule of water and liberating oxygen which escapes at the anode. The cation of the base moves over to the cathode, gives up its charge, and then reacts with water, reforming the base and liberating hydrogen which escapes.

In the electrolysis of a *salt*, the cation moves over to the cathode, gives up its positive charge, then reacts with water liberating hydrogen gas which escapes. The anion moves over to the anode, gives up its charge, and reacts with water liberating oxygen.

It is a very simple matter to show that this older theory is untenable. Take the case of an acid. The anion goes over to the anode, gives up its charge, and then "reacts with water." Just what does this mean? In the case of nitric acid, the anion, $\overline{\mathrm{N}}\mathrm{O}_3$, finds around the anode hydroxyl anions $(\mathrm{O}\overline{\mathrm{H}})$ from the dissociated water. Which will give up its charge? Obviously the one that holds it less firmly. The old theory said that the $\overline{\mathrm{N}}\mathrm{O}_3$ gives up its charge because it holds it less firmly than the hydroxyl, than takes the charge from the hydroxyl, which must hold its charge more firmly than $\overline{\mathrm{N}}\mathrm{O}_3$, otherwise hydroxyl and not $\overline{\mathrm{N}}\mathrm{O}_3$ would have given up its charge. This is, of course, a *reductio ad absurdum.*

The same applies to the older theory of the electrolysis of a base. The cation going to the cathode finds there hydrogen cations from the dissociated water. The cation of the base gives up its charge and not the hydrogen, because the latter holds its charge more firmly than the former. The cation of the base, having been discharged, takes the charge from the hydrogen, which must have held its charge more firmly than the cation of the base, otherwise, the hydrogen and not the cation of the base would have given it up originally. The same absurdity manifests itself as in the case of an acid.

With a salt the old theory leads to an absurdity at both the cathode and the anode. The cation of the salt goes to the cathode and gives up its charge because it holds the charge less firmly than the hydrogen ions from the dissociated water. It then reacts with water, which means that it takes the charge from the hydrogen ions, which is, of course, impossible. The anion of the salt goes to the anode, gives up its charge, because it holds it less firmly than the hydroxyl anion from the dissociated water, then takes the charge from the hydroxyl anion — which is, again, impossible.

It is thus comparatively simple to show that the older theory of electrolysis, based upon the views of Clausius, is in error. It is a very different matter to show what the correct view is. This, however, has been done.

The Decomposition Values of the Ions. — It will be seen from the above that the fundamental question is, which ions hold their charges more firmly, the hydrogen and hydroxyl from the dissociated water, or the anions and cations of acids, bases, and salts? The question has been answered directly and very satisfactorily by Le Blanc,[1] who measured the so-called discharging values of the ions. What does this mean? The discharging value of an ion is the voltage which is necessary and just sufficient to cause the ions in question to lose their charge. This is obviously the voltage which is necessary and just sufficient to cause a continuous current to flow through the solution containing the ions in question.

The results that were obtained will be given in connection with, or as necessary consequences of, the theory which was proposed to account for them.

Newer Theory of Electrolysis. — In the electrolysis of an *acid*, the hydrogen cations, together with the hydrogen ions from the dissociated water, move to the cathode, give up their charges and escape. The anions of the acid move to the anode and find around this pole hydroxyl anions from the water. Which will discharge? Obviously the one which holds its charge less firmly. Le Blanc has shown that hydroxyl has a lower discharging value than almost any other anion except perhaps chlorine, bromine, and the like. Therefore, whenever we electrolyze almost any acid other than the halogen acids, only oxygen is given off at the anode. The hydroxyls from the dissociated water discharge at the anode, two of them combine and liberate oxygen in the usual way, and the anion of the acid simply remains paired off against a hydrogen ion which may have come either from the dissociated water or from the acid.

The consequences of this are very interesting and can readily be tested by the results of experiment.

Newer Theory and Decomposition Values. — If the above suggestion is correct, the *decomposition values of solutions of the strong acids having the same concentrations*

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[1] *Zeit. phys. Chem.*, **8**, 299 (1891).

must be constant. The reason for this is obvious. The decomposition values of such solutions of such acids are simply the voltages which are just necessary to decompose hydrogen and hydroxyl ions of the concentrations at which they exist in the solutions in question. But since these solutions, being of the same concentrations, have the same concentrations of both hydrogen and hydroxyl ions, we have in them the same numbers of the same kinds of ions, and they must, of course, have the same decomposition values. The following results show that the above conclusion is in accord with the facts. These results were obtained for normal solutions.[1]

Acid	Decomposition values
d-Tartaric	1.62 volts
Perchloric	1.65 "
Malonic	1.69 "
Dichloracetic	1.66 "
Monochloracetic	1.72 "
Nitric	1.69 "
Sulphuric	1.67 "

The approximate constancy of these decomposition values is in keeping with the above conclusion.

In the case of bases, the new theory says that the hydroxyl anions move to the anode, give up their charge and react with one another forming water and liberating oxygen. Only hydroxyl ions discharge at the anode. Most of these come from the base, a few from the dissociated water.

The cation of the base goes to the cathode and finds there hydrogen ions from the dissociated water. Le Blanc has shown that hydrogen has a lower discharging value than most of the cations of bases. Therefore hydrogen is liberated. The salts of certain metals, such as copper, yield a cation with a low discharging value, and in such cases, in addition to the hydrogen liberated, we have the metal separating on the cathode.

What has been said above, however, holds in general. The hydrogen ions are discharged at the cathode. If we use the same concentrations of the different strong bases, we have approximately the same concentrations of hydrogen ions around the cathode, and hydroxyl ions around the anode, regardless of the base that we use. The electrolysis of normal solutions of bases is therefore the decomposition of hydrogen and hydroxyl ions at the concentrations at which they exist in these solutions. The *decomposition values of normal solutions of bases should therefore be a constant.* This conclusion is also readily tested by the results obtained by Le Blanc.[1]

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[1] *Zeit. phys. Chem.*, 8, 315 (1891).

Base	Decomposition value
Sodium hydroxide	1.69 volts
Potassium hydroxide	1.67 “
Ammonium hydroxide	1.74 “
$\frac{n}{4}$ Methylamine	1.75 “
$\frac{n}{4}$ Diethylamine	1.68 “
$\frac{n}{8}$ Tetraethyl ammonium hydrate	1.74 “

The conclusion is borne out by the facts.

One other relation should be pointed out while considering acids and bases. In a normal solution of a strong acid the concentration of the hydrogen ions is the same as the concentration of the hydroxyl ions in a normal solution of a strong base. The hydrogen ions in the acid are equal in number to the hydroxyl ions in the base.

The hydroxyl ions in the acid solution coming from the dissociated water are equal in number to the hydrogen ions in the solution of the base which also come from the dissociated water. Since both solutions contain the same number of hydrogen ions and the same number of hydroxyl ions, the *discharging values of the two must be the same,* and the above results show this to be the case.

Let us now consider the electrolysis of salts. The cation of the salt moves to the cathode, and the hydrogen there from the dissociated water discharges. The cation remains around the cathode, paired off against the hydroxyl ion which comes from the same molecule of water as the hydrogen ion. The anion of the salt moves to the anode, the hydroxyl there from the dissociated water discharging. The anion remains paired off against the hydrogen ion which came from the same molecule of water as the hydroxyl ion which has discharged. There is thus an accumulation of hydroxyl anions around the cathode and of hydrogen cations around the anode. What will be the effect of this on the dissociation of water?

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[1] *Zeit. phys. Chem.*, **8**, 315 (1891).

There is a well-known general principle, that the presence of any ion drives back the dissociation of any electrolyte yielding that ion. Therefore, the presence of hydroxyl ions around the cathode and of hydrogen ions around the anode, drives back or diminishes the dissociation of the water around both of these poles. There being a smaller number of ions to discharge, it will require a higher voltage to discharge them, the decomposition values depending not only on the *nature* of the ions, but also on their *number*.

Salts should therefore have higher discharging or decomposition values than either acids or bases. We see that such is the case.[1]

Salts	Decomposition values
Potassium sulphate	2.20 volts
Sodium sulphate	2.21 "
Potassium nitrate	2.17 "
Sodium nitrate	2.15 "
Potassium chloride	1.96 "
Sodium chloride	1.98 "
Ammonium nitrate	2.08 "
Ammonium sulphate	2.11 "
Calcium chloride	1.89 "
Calcium nitrate	2.11 "

The facts are in keeping with the conclusions from theory.

Thus we see that all of the conclusions from the above theory of electrolysis are borne out by the experimental results. We can, therefore, regard this theory as experimentally verified, and can accept it tentatively until some one suggests another theory which harmonizes better with the facts.

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[1] Le Blanc: *Zeit. phys. Chem.*, **8**, 311 (1891).

Electrolysis of Water a Direct Decomposition by the Current. — It may at first sight seem that there is really very little difference between the older theory of electrolysis which is now regarded as untenable, and the newer view supported by the decomposition values found by Le Blanc. A moment's thought will show that such is not the case.

The older theory maintained that the decomposition of water in electrolysis was *not the direct action* of the current, but was a *secondary act.* The direct products of electrolysis, the discharged cations and anions of electrolytes, reacted with the water decomposing it, liberating hydrogen at one pole and oxygen at the other. The decomposition of the water, in terms of the older theory of electrolysis, was then a secondary act, not brought about by the current at all, but by the products of the direct action of the current.

The newer theory of electrolysis is exactly the reverse. The hydrogen ions of the dissociated water are discharged at the cathode, and the hydroxyl ions of the dissociated water at the anode. The *water is decomposed directly by the current,* and this theory of electrolysis is sometimes known as the theory of the primary decomposition of water.

The discharging values of the ions are also the basis of electrolytic separation of the metals, which is a new and comprehensive branch of analytical chemistry, but it would lead us too far to discuss it in any detail here.

PROPERTY OF SOLUTIONS OF ELECTROLYTES TO CONDUCT THE ELECTRIC CURRENT

Solutions of electrolytes differ from those of non-electrolytes in that the former conduct the current while the latter do not. Indeed, this is the fundamental distinction between these two great classes into which all chemical compounds fall.

The power of acids, bases, and salts to conduct the current in aqueous solution must be regarded as among the most fundamental and important properties of solutions of these substances. It not only distinguishes the electrolytes from the non-electrolytes, but the study of this property has done much to throw light on the nature of solution in general. Some stress will therefore be laid on the measurements of conductivity, and on the discussion of the results obtained.

Principle Involved in Measuring Conductivity. — In determining the conductivity of a piece of metal, we must define the size and shape of the piece which we would study, since resistance, and consequently conductivity, is a function of the diameter and length, as well as of the nature of the substance itself. In the case of metals, we may take a cube of the metal whose edge is a centimeter in length; but since this would have very small resistance, and, therefore, great conductivity, it is better to take a cylinder of the metal one meter in length and with a cross-section of one square millimeter. The latter would have $100 \times 100 = 10^4$ times the resistance of the former, and therefore, only one ten thousandth of the conductivity of the cubic centimeter of metal.

In the case of solutions we must choose some standard for the solution to be measured. The conductivities of solutions are far less than those of metals, so we take as a standard the conductivity of a cube of the solution whose edge is one centimeter.

In order that the results for different substances should be comparable, we must deal with comparable numbers of molecules or the ions resulting therefrom, and we must be able to measure the conductivities of solutions of any and all concentrations.

The conductivity of the cube of solution referred to above we will call the specific conductivity and will represent this by c. If we represent the number of cubic centimeters of the solution in question which contain a gram-molecular weight of the substance by p, then the molecular conductivity, which is sometimes called λ, but more frequently μ, will be

$$\lambda \text{ or } \mu = pc$$

The Kohlrausch Method of Measuring Electrical Conductivity. — To determine the molecular conductivity, μ, of any solution, we must be able to determine c, or its conductivity, which is the reciprocal of its resistance, the quantity measured. Kohlrausch has devised a very satisfactory method for measuring the conductivity of solutions.

When a continuous current is passed through a solution, electrolysis results, hydrogen separating at one pole and oxygen at the other. The poles become covered with gases, or they become polarized, as we say. Kohlrausch overcame this difficulty by using not a continuous, but an alternating current. Such a current from a small induction coil was sent through the solution placed in a glass cup containing two platinum electrodes, thrown into one arm of a wheatstone bridge, and a rheostat or resistance box thrown into the other arm. The balance was established by means of a telephone receiver placed one arm between the solution and the rheostat, and the other attached to the bridge by a sliding contact which is moved along the bridge wire until the hum of the inductorium is no longer heard in the telephone. Instead of a telephone receiver a dynamometer or alternating current galvanometer may be employed.

The calculation of the resistance offered by the solution is very simple indeed. If we represent the conductivity referred to molecular quantities as is usually done by μ_v, v being the volume of the solution or the number of liters of the solution that contain a gram-molecular weight of the acid, base, or salt; we have from the principle of the wheatstone bridge

$$\mu_v = \frac{Kvm}{\Delta n}$$

K being the constant of the cell which depends for its value on the size of the electrode plates and the distance they are apart, m and n the readings on the bridge and Δ the resistance in ohms in the rheostat.[1]

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[1] For further details in connection with the deduction of this equation see the Author's *Elements of Physical Chemistry*, 4th edition, p. 392 (The Macmillan Co.).

Applying the Kohlrausch Conductivity Method. — There are two quantities in the conductivity equation which cannot be determined directly by separate experiments. These are μ_v or the molecular conductivity which is the value desired, and K the cell constant. Whenever we have only one equation and two unknown quantities we must by some means eliminate one of the unknowns. In this case we eliminate K, *i.e.*, the cell constant.

This was done for the first cell by measuring the size of the plates and their distance apart. Now that we know the value of μ for many substances it is not necessary to proceed in this way. To "standardize" a cell or determine the "cell constant," we now proceed as follows. We take a solution of some substance whose molecular conductivity at the dilution and temperature is known. We place it in the cell, bring it to the desired temperature, and then determine the other values in the equation, the lengths of the bridge arms, and the resistance in the rheostat, by direct readings. We now have only one unknown in the equation — the cell constant K, and we solve for this. We usually use a $\frac{n}{50}$ solution of potassium chloride, which has a molecular conductivity of 129.7 Siemen's units or 137.9 ohms (reciprocal ohms) at 25°.

The question of the purity of the water used in preparing the solutions whose conductivities are to be measured is fundamental. What we actually measure is the conductivity of the solution plus that of the water, and we must make the latter as small as possible. We then subtract the conductivity of the water from the total conductivity found, and the remainder is the conductivity of the solution in question.

It might seem from this that the actual value of the conductivity of the water used was of very little significance. It would be only necessary to determine the conductivity of the water, whatever it might be, and then subtract this from the total conductivity, in order to get the conductivity of the solution. A moment's thought will show that this will not do. Suppose we are measuring the conductivity of an acid, and the water used contains ammonia. We are then really measuring to some degree, not the conductivity of the acid, but of its ammonium salt. The conductivity of the ammonium salt of any acid is only a small part of the conductivity of the acid itself, because the ammonium ion moves far more slowly than the hydrogen ion. The values that we would thus obtain would bear no direct relation to the values that we wish to secure.

If the substance whose conductivity we were measuring was a base, and the water used contained carbon dioxide, we would to some extent be measuring the conductivity of the carbonate of the base. The carbonate would have far less conductivity than the free base, because the $\overset{=}{\mathrm{C}}\mathrm{O}_3$ ion moves so much more slowly than the hydroxyl ion. The results obtained would, therefore, have no real significance.

Purification of Water. — Pure water has never been prepared. For that matter, nothing has ever been prepared pure, and nothing ever can be while the present laws of nature obtain; since everything is soluble in everything else with which it comes in contact. The purest water has been prepared by Kohlrausch and Heydweiller,[1] and in the following way. Water which had been purified by distillation was subjected to fractional crystallization, and the purification carried as far as possible by this process. It was then placed in one arm of a *U*-shaped platinum vessel which was attached to an air-pump. After removing the air, a part of the water was distilled from one arm of the vessel over into the other. Into the receiving arm electrodes had been inserted, and the conductivity of the water determined without allowing it to come in contact with the air.

The easiest way to remember the value of the resistance or conductivity of water thus purified, is as follows. The electrical resistance of a millimeter cube of this water at zero is the same as that of a copper wire whose cross-section is a square millimeter, the length of the wire being such that it could be *wrapped around the earth at the equator one thousand times*. Such water would be ideal for conductivity work, but it is next to impossible to obtain water of this degree of purity in any quantity, and further, if such water could be obtained in quantity, it could not be preserved with this degree of purity during use for conductivity purposes.

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[1] *Zeit. phys. Chem.*, **14**, 317 (1894).

We must then devise a method for obtaining water of purity sufficient for conductivity work, and in fairly large quantity. A number of such methods have been devised. The one used in this laboratory consists in distilling ordinary distilled water from chromic acid, and then redistilling the product from barium hydroxide. The chromic acid burns up the organic matter in the water and holds back the ammonia. The carbon dioxide which passes over is "fixed" by the barium hydroxide, and the product is pure enough for conductivity purposes. By this method about ten liters of water a day may be obtained, having a specific conductivity of about 1×10^{-6}.

Regulation of Temperature — We shall see that the conductivities of solutions of electrolytes increase enormously with rise in temperature. This is exactly the reverse of what takes place with metals. The conductivities of the latter decrease with rise in temperature, or increase with fall in temperature; becoming infinite at or near absolute zero, as has recently been shown experimentally by Kammerlingh Onnes.

The temperature coefficients of conductivity of solutions of electrolytes are as much as several percent per degree rise in temperature. Therefore the temperature must be very accurately regulated in making conductivity measurements.

A large number of regulating devices have been proposed for this purpose. The Ostwald[1] regulator did good service in its day. Better forms, however, are now available.[2]

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[1] *Zeit. phys. Chem.*, **2**, 565 (1888).

[2] *Carnegie Institution of Washington*, Publication No. **198**, Chap. III (1914); No. **210**, Chap. VI (1915). *Journ. Amer. Chem. Soc.* **38**, 516 (1916).

Some Results of Conductivity Measurements. — An examination of the conductivity results thus far obtained will show that, with respect to their power to carry the electric current, electrolytes fall into three classes. First, strong acids, which have the greatest conductivities; second, strong bases, which have intermediate conductivities; and third, salts, which have the smallest conductivities. We can readily understand why the electrolytes fall in this order. The acids yield the hydrogen ion, which is the swiftest of all the ions and therefore gives the largest conductivity. The bases yield the hydroxyl ion, and this, next to the hydrogen, is the swiftest of all the ions. The ions of the salts move with very much smaller velocities than the hydrogen and the hydroxyl ions, and, therefore, the conductivities of the salts are very much less than those of the strong acids and the strong bases.

Among the acids very different degrees of conductivity are represented. The strongest acids are the best conductors of all the electrolytes, as has been stated; but we have all degrees of conductivity represented by the different acids. We have aqueous solutions of such acids as hydrocyanic, carbonic, boric, which are scarcely electrolytes at all. We have solutions of the organic acids which have conductivities all the way from very small to very large values; the strongest organic acids having conductivities of the same order of magnitude as the strong mineral acids.

Among the bases we also have many degrees of conductivity represented. We have many examples of very weak bases such as ammonia and its derivatives. We also have the very strong bases — the hydroxides of the alkalies, and also bases with intermediate conductivities. None of the salts are as good conductors as the strongest acids and bases, but they are, in general, good conductors of electricity. Nearly all of the salts are strongly dissociated compounds, and therefore yield in aqueous solution a large number of ions. Even if these ions do not move with such velocities as the hydrogen and hydroxyl ions, their large numbers give the solutions high conductivities. There are a few exceptions to the aqueous solutions of the salts being good conductors. The halogen salts of mercury in aqueous solution are nearly non-electrolytes. These solutions have almost no conductivity at all. The same applies in a much less degree to the halides of cadmium and zinc. The meaning of these facts is at present entirely unknown.

For any given electrolyte the molecular conductivity usually increases with the dilution of the solution until a certain maximum value is reached. From this point on the molecular conductivity has the maximum, constant value.

There are, however, many exceptions to this statement, as Sachkanov[1] has shown. Certain substances, in solvents with small dielectric constants, show an increase in the molecular conductivity with increase in the concentration of the solution. This is accounted for by Sachanov as due to the polymerization of the solute in such solvents, especially in the more concentrated solutions, with the formation of complex molecules which are more highly dissociated than the simpler molecules.

Law of Electrical Conductivity. — The fundamental law of the electrical conductivity of aqueous solutions of electrolytes was discovered by Kohlrausch, who devised the method now almost universally used for such work. The general statement of the law is this. Each *ion moves with its own definite velocity which, in any given solvent, and under a constant driving force, is constant.* This velocity does not depend on the nature, number, or condition of the other ions present in the same solution. If we represent the maximum molecular conductivity for any substance, already referred to, by μ_∞, the molecular conductivity at infinite dilution, we would have —

$$\mu_\infty = K_c + K_a$$

K_c being a constant dependent for its value upon the nature of the cation, and K_a a constant dependent for its value upon the nature of the anion. Ostwald has generalized this law of Kohlrausch, extending it from solutions of infinite dilution to solutions of all dilutions. The difference between a very dilute solution and one more concentrated, from the present standpoint, is that the former is completely dissociated while the latter is only partly broken down into ions. In attempting to apply this law to solutions in general, the dissociations of these solutions must be taken into account; and this is just what Ostwald did. He showed that if the dissociation of the solution in question is multiplied into the above equation, the Kohlrausch law can be applied to solutions of electrolytes in general. Calling the percentage of dissociation α, we have,

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[1] *Zeit. Elektrochem,* **20**, 529 (1914).

$$\mu_v = \alpha(K_c + K_a)$$

Dissociation of Electrolytes Measured by the Conductivity Method. — The chief scientific use of the conductivity method is to measure electrolytic dissociation. This application is theoretically very simple. If the solution is not dissociated it does not conduct. If the dissociation is complete, the conductivity is greater than at any other dilution, as we are dealing with molecular quantities. If the dissociation is somewhere between zero and one hundred percent, the conductivity of the solution will be between zero and its greatest value. Since conductivity is proportional to dissociation, the dissociation at any dilution is simply the ratio between the molecular conductivity at the dilution in question and the maximum value of the molecular conductivity. If we represent this, as is usually done by μ_∞, we have the dissociation α:

$$\alpha = \frac{\mu_v}{\mu_\infty}$$

To find μ_∞ for strong electrolytes, it is only necessary to increase the dilution of the solution until complete dissociation is reached, and then determine the molecular conductivity of such a solution which is the value of μ_∞ desired.

In case the compound in question is only weakly dissociated, as with weak acids and weak bases, we cannot determine μ_∞ directly by the method just discussed. The dilution of the solution in which μ_∞ is reached is so great, that the conductivity method cannot be applied to it. In such a solution the solvent would conduct more than the dissolved substance.

For such substances an indirect method[1] of determining μ_∞ has been worked out, which is very efficient, but which would lead us too far to discuss it in any detail.

Relation Between Dissociation and Dilution. — It has been known from the time that the dissociation theory was proposed, that the dissociation of solutions increases with the dilution of those solutions. There is a dilution at which any electrolyte is completely dissociated. This knowledge was purely qualitative. What we want to know is, how much does the dissociation of a solution increase for a given increase in its dilution? What is the relation between the rate of increase in the dissociation and the rate of increase in the dilution?

This question was first answered by Ostwald, in what has come to be known as his dilution law. Connecting these two quantities, dissociation and dilution, he deduced the following expression.[2]

$$\frac{\alpha^2}{(1-\alpha)v} = \text{constant}$$

in which α is the percentage dissociation of the solution, and v the volume of the solution, or number of liters, that contains a gram-molecular weight of the electrolyte.

This dilution law of Ostwald was found to hold for solutions of weakly dissociated acids and bases; but did not hold for a single strongly dissociated compound. Very good constants were obtained for a large number of weak acids and weak bases, varying the dilution of the solution over a wide range, and these constants are very significant. Given the "constants" of the acids and bases, we know the relative strengths of these substances. Knowing their relative strengths, we know exactly what these acids and bases will do chemically under any given set of conditions. We know with what substances they will react, and how rapidly. We know, further, the conditions of equilibrium when more than one of these compounds is involved. In a word, knowing the "constant" of an acid or a base, we know its physical chemistry. We obtain the "constant" simply by measuring the dissociation of the substance over a range of dilutions, and this is quickly and easily done. Physical chemical methods thus enable us to learn more about acids as acids, and bases as bases, in a very short while, than we could learn in a lifetime through the application of chemical methods alone. The Ostwald dilution law has a good physical basis upon which it rests, and from which it is deduced by the only rigid scientific method, *viz.*, the mathematical. Unfortunately it applies to only weak acids and weak bases, but why this limitation we do not know. There is, however, another expression which holds for strong acids and strong bases, and which does not hold for the weakly dissociated compounds. This expression, which is purely empirical and apparently has no physical basis at all, was found by Rudolphi.[1]

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[1] See Author's *Elements of Physical Chemistry*, 4th edition, p. 406. (The Macmillan Co.)

[2] *Zeit. phys. Chem.*, **3**, 170, 241, 369 (1889). See also Author's *Elements of Physical Chemistry*, 4th edition, p. 411. (The Macmillan Co.)

$$\frac{\alpha^2}{(1-\alpha)\sqrt{v}} = \text{constant.}$$

in which α is the percentage dissociation, and v the volume of the solution or the number of liters containing a gram-molecular weight of the electrolyte.

This expression seems to hold for the strongly dissociated electrolytes about as closely as the Ostwald law does for the weakly dissociated compounds. In this expression we find the square root of v, but we have at present no conception of its meaning. Other equations connecting dilution and dissociation were found by Van't Hoff,[1] and by Kohlrausch,[2] and by Krause.[3] These are again more or less empirical and need not be discussed in detail in the present connection.

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[1] *Zeit. phys. Chem.*, **17**, 385 (1895).

Conductivity and Dissociation at Elevated Temperatures. — We have seen that the conductivities of electrolytes have large temperature coefficients, and that these coefficients are positive. This means that conductivity increases rapidly with rise in temperature. We can measure the conductivities of aqueous solutions in open vessels obviously only up to one hundred degrees. To study this property at still higher temperatures, closed vessels must be used. A convenient bomb for this purpose has been devised by A. A. Noyes and co-workers. A steel bomb lined with platinum, into which properly insulated electrodes had been sealed, was employed for this purpose. The temperatures chosen were the boiling-points of certain liquids which could readily be obtained reasonably pure. They were, 18°, 100°, 156°, 218°, 281°, and 306°, and later work was at even higher temperatures.

A few of the results[4] obtained for a few compounds are given to show the rate at which the conductivity increases with rise in temperature.

Temperature	KCl	NH_4Cl	K_2SO_4	HCl
18°	130.1	130.7	132.8	376.0
100°	414.0	415.0	455.0	850.0
156°	625.0	628.0	715.0	1085.0
218°	825.0	841.0	1065.0	1265.0
281°	1005.0	—	1460.0	—
306°	1120.0	1176.0	1725.0	1424.0

The question arises, what is the effect of rise in temperature on the dissociation of electrolytes? It does not follow that because rise in temperature increases the conductivity of electrolytes, that it also increases their dissociation. This will be seen at once if we remember that dissociation is not proportional to conductivity, but is the ratio between the conductivity at the dilution in question and at infinite dilution:

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[1] *Zeit. phys. Chem.*, **18**, 300 (1895).

[2] *Ibid*, **18**, 662 (1895).

[3] *Zeit. Elektrochem*, **20**, 524 (1914).

[4] Taken from *Carnegie Institution of Washington*, Publication No. **63**, 335 (1907).

$$\alpha = \frac{\mu_v}{\mu_\infty}$$

We have seen that μ_v increases rapidly with rise in temperature, but μ_∞ might increase still more rapidly; in which case the dissociation would be less at the higher temperature. The effect of rise in temperature on dissociation can be answered only by direct measurements of dissociation at different temperatures. This has been done in the same experiments above referred to. Not only were the values of μ_v determined at the different temperatures, but the effect of temperature on the maximum molecular conductivity was also studied.

The effect of rise in temperature on dissociation can be seen from a few results[1] with a few compounds.

Electrolyte	Concentration	18°	218°	306°
HCl	0.01	97.1	92.2	82.0
KCl	0.01	94.2	89.8	81.0
K_2SO_4	0.01	87.2	63.0	37.0
CH_3COOH	0.08	1.50	0.46	0.14
NH_4OH	0.08	1.45	0.47	0.11

The results suffice to illustrate the general effect of rise in temperature on dissociation. The *higher the temperature of the solution the less its dissociation.* The reason for this will appear in the next chapter, where the relation between the dissociating power of solvents and another physical property of liquids will be discussed.

How Electrolytes are Dissociated by Water. — We have seen that the characteristic ion of all acids is hydrogen. This means that all acids dissociate into a hydrogen ion, or into hydrogen ions, which carry the positive electricity, and into something else which carries the negative charge.

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[1] *Carnegie Institution of Washington,* Publication No. **63,** 340 (1900).

The way in which monobasic acids break down is very simple. This is illustrated by hydrochloric acid,

$$HCl = \overset{+}{H} + \overset{-}{Cl}$$

The molecule is simply broken down into one univalent, positive hydrogen ion, and one univalent, negative chlorine ion.

In the case of dibasic acids the dissociation is more complicated. It takes place in two stages. Sulphuric acid, in fairly concentrated solutions, dissociates wholly or in part as a monobasic acid,

$$H_2SO_4 = \overset{+}{H} + \overset{-}{HSO_4}$$

When the dilution of the solution is sufficiently increased we have the second stage of the dissociation, which consists in the dissociation of the $HS\overline{O}_4$ ion, thus,

$$\overset{-}{HSO_4} = \overset{+}{H} + \overset{=}{SO_4}$$

and these two stages in the dissociation of dibasic acids are characteristic of substances of this class.

Tribasic acids dissociate in three stages, as follows—

$$H_3PO_4 = H_2\overset{-}{PO_4} + \overset{+}{H}$$

$$\overset{-}{H_2PO_4} = H\overset{=}{PO_4} + \overset{+}{H}$$

$$\overset{=}{HPO_4} = \overset{\equiv}{PO_4} + \overset{+}{H}$$

Which of these takes place depends upon the dilution of the solution. In solutions of the proper concentrations we may have all three stages going on simultaneously.

When we turn to bases, similar phenomena manifest themselves. A monacid base dissociates thus,

$$NaOH = \overset{+}{Na} + \overset{-}{OH}$$

Diacid bases may dissociate in two stages, thus,

$$Ba(OH)_2 = \overset{+}{BaOH} + \overset{-}{OH}$$

and then, with increase in dilution,

$$\overset{+}{BaOH} = \overset{++}{Ba} + \overset{-}{OH}$$

When we come to salts, the problem of how they dissociate is a very complex one, except for the simple salts, which dissociate about as we would expect them to do,

$$KCl = \overset{+}{K} + \overset{-}{Cl}$$

$$Ba(NO_3)_2 = \overset{++}{Ba} + \overset{-}{NO_3} + \overset{-}{NO_3}$$

$$Na_2SO_4 = \overset{+}{Na} + \overset{+}{Na} + \overset{=}{SO_4}$$

These dissociations may go on in stages with increase in the dilution. But the complex salts dissociate in a variety of different ways.

Take certain complex double sulphates—the alums—$KAl(SO_4)_2$; $NH_4Cr(SO_4)_2$. How do these substances break down in the presence of water? What are aqueous solutions of the alums? This problem was studied by Jones and Mackay.[1] They found that in dilute solution the alums dissociate almost completely into their constituent sulphates, and these are broken down by the water as if they were alone in separate solutions. In brief, the alums in dilute aqueous solution are completely dissociated into their simplest ions thus,

$$KAl(SO_4)_2 = \overset{+}{K} + \overset{+++}{Al} + \overset{=}{SO_4} + \overset{=}{SO_4}.$$

An alum in dilute aqueous solution is therefore not an alum at all, but is simply a mixture of the ions from the two sulphates of which the alum in question is composed. In more concentrated solutions, however, the alums first break down as salts of complex acids, thus,

$$KAl(SO_4)_2 = \overset{+}{K} + \overset{-}{Al(SO_4)_2},$$

and then with increase in the dilution this complex anion undergoes further dissociation.

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[1] *Amer. Chem. Journ.*, **19**, 83 (1897).

The way in which this was proved may be of some interest. The freezing-point lowerings produced by the alum solutions were measured. Also the freezing-point lowerings of the individual sulphates, and the sum of the latter compared with the former. If the alum dissociated as a salt of a complex acid, the sum of the lowerings of the constituents would be *greater* than that of the alum. If the latter dissociated into its simplest ions, just as the constituent sulphates would do, then the sum of the lowerings would just equal the lowering produced by the alum itself.

In all of this work the question of the isohydric or non-isohydric nature of the solutions was taken into account, and the effect of each on the magnitude of the dissociation of the other.

The term isohydric was first[1] applied to those solutions which contain in a given volume the same number of hydrogen ions. The term has now become generic, and means simply two or more solutions which contain the same number of any given kind of ion in the same volume. Thus, two solutions which contain in a given volume the same number of chlorine ions are termed isohydric.

In attacking the above problem the conductivity method was used as well as the freezing-point. The conductivities of the individual solutions of the constituents were measured, and then the conductivities of the alums, and the results compared exactly as their freezing-point lowerings were compared, with the same general result.

The double chlorides, bromides, and iodides were studied by exactly the same methods that had been used with the double sulphates, with the following result. The double halides, as they are termed, dissociate as salts of complex acids in more dilute solutions than do the alums. It requires greater dilution to break down these complexes than in the case of the double sulphates. Thus, the double chloride of potassium and zinc dissociates thus,

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[1] *Wied. Ann.*, **30**, 51 (1889).

$$K_2ZnCl_4 = \overset{+}{K} + \overset{+}{K} + \overset{=}{ZnCl_4}$$

and it requires very great dilution to break down $\overset{=}{ZnCl_4}$ into,

$$\overset{=}{ZnCl_4} = \overset{++}{Zn} + \overset{-}{Cl} + \overset{-}{Cl} + \overset{-}{Cl} + \overset{-}{Cl},$$

What has been said of the double chlorides applies also to the double bromides and iodides. In concentrated solution they tend to dissociate as salts of complex acids, and these complexes are broken down only at very great dilutions.

Ways in which Ions are Formed. — It has been pointed out by Ostwald[1] that ions are formed from molecules in a number of different ways. Ions are formed most frequently by the molecules simply breaking down into an equivalent number of cations and anions. This is the way ions are produced when acids, bases, and salts are dissolved in water and in other dissociating solvents. Nitric acid in the presence of water is dissociated into the hydrogen ion and the $\overset{-}{NO_3}$ anion. All acids are dissociated into the hydrogen ion or hydrogen ions and an anion the nature of which depends upon the acid in question.

As a typical base take potassium hydroxide. It dissociates into the hydroxyl anion and the potassium cation — all bases yielding hydroxyl as the anion.

Salts dissociate into cations and anions, the nature of both depending on the nature of the salt in question.

The second mode of ion formation pointed out by Ostwald is where a metal like zinc displaces copper from a solution of one of its salts, or chlorine displaces the anion iodine from its salts. What takes place in the first case is, the atom of zinc takes the two positive charges from the copper ion, liberating the atoms of copper; the zinc atom, becoming ionic, passes into solution. Similarly, the chlorine atom takes the negative charge from the iodine ion, iodine being set free and the chlorine becoming an anion. Both of these are examples of transference of an electrical charge, and this is the key to all acts of substitution in chemistry, whether organic or inorganic.

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[1] *Lehrb. d. allg. Chemie*, II, 786 (1893).

Other examples of this method of ion formation, cited by Ostwald, are the replacement of gold from solutions of auric chloride by hydrogen gas under pressure; the action of potassium on water, the solution of metals in general in acids, etc.

The third method of ion formation cited by Ostwald is where one neutral substance passes into cations, another neutral substance at the same time passing into anions. The example given is the action of chlorine water on gold. Neither gold nor chlorine alone can become ionic, but when brought into the presence of one another, the one, gold, takes positive charges and becomes cations; the other, chlorine, takes negative charges and becomes anions.

The fourth and, according to Ostwald, the only other simple way in which ions are formed is illustrated by the action of chlorine on ferrous chloride. The ferrous ion with its two positive charges is converted into the ferric ion with three positive charges; the chlorine atom being converted into the chlorine anion. This is oxidation in that sense of the term oxidation which means simply raising the valence — an unfortunate use of the term, which should be reserved for those chemical processes involving the addition of oxygen.

The same mode of ion formation is illustrated by the action of chlorine on a solution of potassium manganate. The chlorine atom takes one negative charge from the ion $\mathrm{M\overline{\overline{n}}O_4}$, converting it into $\mathrm{M\overline{n}O_4}$ which is the anion of permanganates; one of the potassium ions from the manganate pairing off against the chlorine ion formed as indicated above.

These are the simple ways in which ions are formed. More than one of these may be operative at the same time and give rise to relatively complex processes. However, it is not necessary to consider these more complicated reactions in any detail, having in mind the simple principles underlying them.

VELOCITIES WITH WHICH THE IONS MOVE

Faraday's law states that when the electric current is passed through solutions of electrolytes, the ions move to the poles — the cations to the cathode and the anions to the anode. The question that arises in this connection is, how rapidly do these ions move towards the poles?

This involves two questions. First, what are the relative velocities of the different anions and cations, and secondly, what are their actual velocities?

Relative Velocities of Ions. — The determination of the relative velocities with which the ions move is based upon the changes in the concentrations of the solutions around the poles, when the current is passed through the solution. The change in the concentration of the original solution around the cathode, divided by the amount of the electrolyte decomposed, gives the relative velocity of the anion. The change in concentration around the anode, divided by the amount of the electrolyte decomposed, gives the relative velocity of the cation.[1] The important point experimentally is to use a form of apparatus[2] which will allow a complete quantitative separation of the solutions around the two poles, after the electrolysis is completed.

Apparatus designed by the Author. — A form of apparatus which was found to work very satisfactorily, is sketched in figure 5. The solution is placed in the side tubes, which are connected with a large siphon carrying a large stop-cock. The two electrodes are inserted into the two side tubes, as shown in the drawing. The current is passed until enough change in concentration around the poles is produced to be measured with accuracy, and at the same time to leave some unaltered solution in the tops of these tubes. When the current is cut off the stop-cock is closed, the solutions removed from the two sides and analyzed; the two sides of the apparatus having been calibrated in advance.

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[1] *Amer. Chem. Journ.*, **32**, 409 (1904); **36**, 427 (1906).

[2] See Author's *Elements of Physical Chemistry*, 4th edition, p. 379 ff. (The Macmillan Co.)

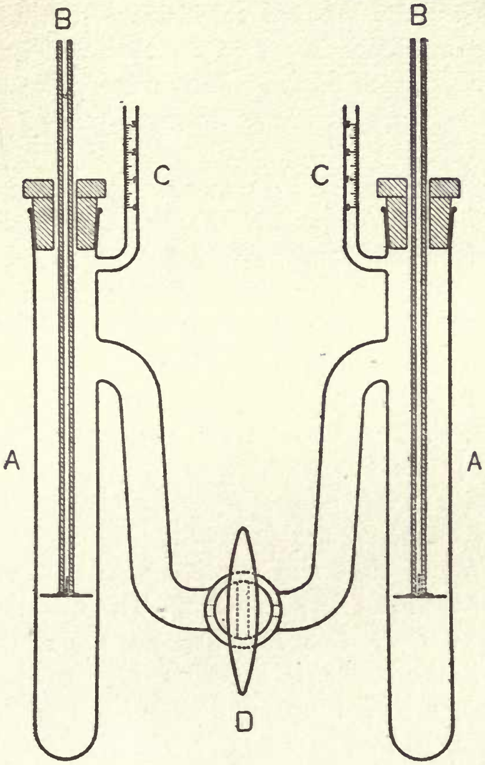

Fig. 5

To ascertain how much of the electrolyte has been decomposed by the current, the amount of current passed is determined by inserting a voltmeter in its path. Knowing the amount of electricity that was passed through the solution, from Faraday's law we can calculate directly the amount of the electrolyte decomposed. Knowing the change in the concentration of the electrolyte around each of the poles, and the total amount of the electrolyte decomposed, we have all the data necessary for calculating the relative velocities of the ions.

Certain conditions have to be observed in this work, such as the strength of the solution used, the temperature at which the work is done, the strength of the current employed, etc.

It should be stated that in all such work very small currents should be used. If the current is large, heating effects result which tend to mix the altered with the unaltered portion of the solution. Therefore, currents of only a few thousandths of an ampere are used.

Effects of Concentration and Temperature. — The questions of the concentration of the solution and of the temperature, in their effects on the relative velocities of the ions, are of interest in connection with certain work which has been done in this laboratory and which will be discussed in the later chapters of this book.

It was found that the relative velocities change with the concentration of the solution. The question is, why? There are at least two reasons. In the first place the viscosity of the solvent becomes less with increase in dilution. This would affect differently the velocities of the two ions, if these ions have, as they usually do, different volumes and different masses. When we take into account the change in hydration in aqueous solutions with change in concentration, as is done in the later chapters of this work; and further, that there is a different change in the hydration of the cation and of the anion with change in concentration; we can see how the relative velocities of the cation and the anion would be changed with change in the concentration of the solution. The rule in such work is to use a solution so dilute that, when the dilution is still further increased, the relative velocities remain constant.

The effect of temperature on the relative velocities of the ions was, for a long time, a puzzle. It was early shown by Loeb and Nernst,[1] that the effect of rise in temperature is to *cause all the ions to have the same velocity.* The explanation of this rather surprising fact was, for a long time, not forthcoming. The explanation today seems to be perfectly simple. The effect of rise in temperature, as we shall see in later chapters, is to cause the hydrates around the ions in water, and the solvates around the ions in solvents in general, to become simpler — the tendency of rise in temperature is to *de-solvate* the ions. Since the different ions have very different powers to combine with the molecules of any given solvent, when these ions are even partially de-solvated, they would have more nearly the same volumes and the same masses, than when they were solvated to a greater extent.

We must further take into account the fact, that with rise in temperature the viscosities of solvents become less and less. Taking both of these facts into account, we can see why rise in temperature would tend to equalize the relative velocities with which the different ions move.

Results of Measurements of the Relative Velocities of the Elementary Ions. — It was early found that the swiftest of all the ions is hydrogen. This, it will be remembered, is the characteristic ion of acids, is common to all acids, and always shows acidity. Further, it is one of the constituents of water, combining with the hydroxyl ion to form water.

Next to hydrogen the hydroxyl ion is the swiftest. Its velocity is a little more than half that of the hydrogen ion. It should be recalled that hydroxyl is the characteristic ion of all bases. It is worthy of note that the characteristic ions of acids on the one hand, and of bases on the other, are the swiftest of all the ions, and not only the swiftest, but very much the swiftest, as the following results will show. These results are taken from the work of Bredig.[1]

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[1] *Zeit. phys. Chem.*, **2**, 962 (1888).

Element	Atomic weight	Velocity
Caesium	132.81	73.6
Rubidium	85.45	73.5
Potassium	39.14	70.6
Sodium	23.00	49.2
Lithium	6.94	39.8
Barium ½	137.37	64.0
Strontium ½	87.63	63.0
Calcium ½	40.07	62.0
Magnesium ½	24.32	58.0
Iodine	126.92	72.0
Bromine	79.92	73.0
Chlorine	35.46	70.2
Fluorine	19.0	50.8

The velocity of hydrogen at 25° is 325, and of hydroxyl is 170; thus, we see that the velocity of the hydrogen ion is *several times* greater than that of any other cation, and the velocity of the hydroxyl ion more than twice that of any other anion. The relatively great velocities of the ions of which water is composed thus stand out as among their most striking properties.

Interpretation of the Results. — It is of interest to note that the velocities of the alkalies decrease as the atomic weights decrease. Lithium moves more slowly than sodium, which moves more slowly than potassium, rubidium, and caesium. This is exactly the opposite of what might be expected. The lighter the ion, other things being equal, the faster it would move. The case is even more remarkable, when we consider that the volume of the lithium ion is less than that of sodium; sodium less than potassium; potassium less than rubidium, and rubidium less than caesium.

The lithium ion is not only *lighter* than any other ion of the alkali group, but it is also *smaller*,[2] and both of these facts would tend to make it move more rapidly under a given driving force. The fact is it moves more slowly, and this fact puzzled physical chemists for some time. We have today a perfectly satisfactory explanation of these facts.

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[1] *Zeit. phys. Chem.*, **13**, 242 (1894).

[2] See *Elements of Physical Chemistry*, by the author; 4th edition, p. 29. (The Macmillan Co.)

Lithium ions are strongly hydrated[1] in aqueous solutions, sodium ions less strongly hydrated, while potassium, rubidium, and caesium ions are scarcely hydrated at all. What moves through the solvent is the hydrated lithium ion, *i.e.*, the lithium ion with its attached molecules of water. This complex is probably heavier and has a larger mass than any other alkali ion, and therefore moves more slowly. Similarly, the hydrated sodium ion has a greater mass, and probably a greater volume, than the much less hydrated potassium, rubidium, and caesium ions; and therefore moves more slowly.

When we come to the alkaline earths, we find the same general relations. Magnesium ions are the most strongly hydrated, calcium and strontium next, and barium least, and this is the order of their velocities.

We know at present very little about the hydration of anions. From the above data of relative velocities we would be led to conclude that fluorine is more hydrated than chlorine, which is more hydrated than bromine, which, in turn, is more hydrated than iodine. When the facts are known, it will be interesting to see whether this prediction is verified.

The relation between water of hydration in aqueous solutions of salts, and their ionic volumes, will be discussed in one of the later chapters of this book.

Bredig[2] has plotted the relative velocities of the ions against the atomic weights as a curve, and finds well-defined maxima and minima in the curve. These maxima and minima are analogous to those in the atomic volume curve.[3] The analogy is, indeed, very striking. At the maxima of the atomic volume curve fall the alkali elements, lithium, sodium, potassium, rubidium, and caesium. At the maxima of the ionic velocity curve fall these same elements. This resemblance between the two curves manifests itself for many of the elements other than those referred to above, but this cannot be discussed here in more detail.

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[1] See *Carnegie Institution of Washington*, Publication No. **60**, 31 (1907).

[2] *Zeit. phys. Chem.*, **13**, 243 (1894), also the Author's *Elements of Physical Chemistry*, 4th edition, p. 387. (The Macmillan Co.)

[3] The Author's *Elements of Physical Chemistry*, 4th edition, p. 29.

Actual Velocities with Which the Ions Move. — The question of the relative velocities of the different ions is one thing, and that of the actual velocities of the ions under a given driving force is another. Having determined the relative velocities of the different ions, and the absolute velocity of any one ion, of course, the absolute velocities of all the ions would be known.

Our problem, then, is to determine the absolute velocity of some one ion. We shall see that the fastest ions move very slowly. Therefore, we would naturally choose one of the swiftest ions to measure the absolute velocity, and such has been done. Indeed, the best measurements of absolute velocities of ions have been made on the very swiftest ion, hydrogen.

The method we owe to the English physicist, Lodge.[1] We mean by the velocity of an ion the same that we mean by the velocity of any moving body — the distance traveled in a given time. How far does the hydrogen ion travel under a given driving force, in unit time? The apparatus and method used by Lodge are the following.

Two beakers were connected with a graduated siphon, and into each beaker a platinum electrode was plunged. Sulphuric acid was poured into the two beakers, and the connecting siphon was filled with jelly containing sodium chloride to which just enough alkali was added to show the alkaline reaction with phenolphthalein which was also dissolved in the jelly. In Lodge's own words, "To detect the motion of *hydrogen*, Mr. Robinson devised the following arrangement: — We happened to have been using phenolphthalein as a detector of alkali in some other quite distinct experiment, and so it was a handy substance. The jelly tube contains a little phenolphthalein and a trace of common salt, just made alkaline enough with soda to bring out the color. The solution in the anode vessel is H_2SO_4; in the cathode vessel the same, or sometimes $CuSO_4$.

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[1] *Brit. Ass. Report*, 1886, p. 393.

"The result is that SO_4 travels one way, and H the other. As the H travels, it liberates HCl, and decolorizes the solution by forming neutral Na_2SO_4. The velocity of hydrogen, for 40 volts applied to a 40 centimeter tube, came out from the very first observation thus made as 0.0029 centimeters per second. Kohlrausch's theoretical number, deduced from conductivity and migration data, is 0.003. Later experiments gave respectively .0026 and .0024. SO_4 seems to travel at about one-third this speed."

So much for Lodge's method and for the results obtained by him. For a potential drop of one volt per centimeter, along the tube, the hydrogen ion, the swiftest of them all, moves with a velocity of about three-thousandths of a centimeter per second; and the other ions with velocities which bear the relation to this, of the relative velocity of the ion in question to the relative velocity of the hydrogen ion. Thus, chlorine and potassium, which have practically the same velocities, have under the conditions of the Lodge experiment, an absolute velocity of $\frac{70}{825}$ of 0.003 cm. per second; and, in a similar manner, the absolute velocities of any other ion whose velocity relative to hydrogen is known, can be calculated.

We thus see that the swiftest ions move very slowly indeed, even under a strong driving force.

Velocities of Ions and of Gaseous Molecules. — It is interesting to compare the velocity of the hydrogen ion in solution under an electrical force of a potential drop of a volt per centimeter, with the velocity of the gaseous hydrogen molecule under normal conditions. We have seen that under the conditions of the Lodge experiment, the hydrogen ion moves only 0.003 cm. per second. The hydrogen molecule in hydrogen gas, under normal conditions of temperature and pressure, moves with a velocity of over a mile a second — the velocity being of an entirely different order of magnitude from that at which the hydrogen ion travels.

This comparison is of interest in connection with the relations between the gas-pressure of a gas and the osmotic pressure of a dissolved substance, which have already been pointed out (p. 72). We know the cause of gas-pressure. It is explained by the kinetic theory. It is due to the gas-particles striking against the walls of the containing vessel. The attempt was made by Van't Hoff[1] to explain osmotic pressure in a similar kinetic way. The attempt, however, was not successful; and no other kinetic theory of osmotic pressure thus far proposed can be regarded as explaining osmotic pressure at all satisfactorily.

ELECTROMOTIVE FORCE OF PRIMARY CELLS

One of the most important scientific applications of the relations between solutions and gases and of the theory of electrolytic dissociation, is to the problem of the electromotive force of primary cells.

The primary cell was discovered by Galvani and constructed by Volta more than one hundred years before its action was understood. A typical primary cell consists of two metals, each surrounded by one of its own salts; the metals being connected with each other, and the two solutions connected through a siphon filled with the one or the other solution.

What is the source of the electromotive force in such an element, or what are the sources of the electromotive force? There are several possibilities, and widely different views have been held concerning the action of the primary cell. Some have supposed that the chief sources of the electromotive force were at the surfaces of contact of the electrodes with the electrolytes. Others, that the main action of the primary cell was at the contact of the two electrolytes with one another; and still others, that the source of most of the electrical energy was at the contact of the two metals with one another.

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[1] *Zeit. phys. Chem.*, 1, 481 (1887).

The problem of the primary cell as a unit — as a machine — was dealt with by Willard Gibbs in this country, and by Helmholtz in Germany, on thermodynamical grounds.

The simplest form of primary cell consists of two electrodes of same metal plunged into solutions of a salt of the metal, the two solutions around the two electrodes having different concentrations.

Gibbs and Helmholtz were able to establish a relation between the electrical energy which appears in such a cell, and the heat energy required to produce equality of concentration on the two sides by distilling water from the more dilute into the more concentrated solution until the two concentrations were equal.

This was an important step in the solution of the problem of the primary cell, but it dealt with the cell as a whole. It did not go into the cell, as it were, and show how it acted. It did not analyze the cell and show how much of the electromotive force came from one source and how much from another. This was done by the application of what was learned about solutions by Van't Hoff and Arrhenius; by the application of the gas laws to solution and the dissociation theory to the problem in hand.

This application we owe to Nernst.

Solution-Tension of the Metals. — Nernst introduced a conception, new at the time, which he called the *electrolytic solution-tension of the metals*. In a word, it is this. When a bar of metal is immersed in a solution of one of its own salts (or into other solutions or solvents), there is at its surface a tension or pressure which tends to drive the metal atoms in the form of ions off the bar into the solution.

Opposing the solution-tension of the metal is the osmotic pressure of the ions in the solution. In some forms of cells it is the osmotic pressure of the cation which is operative; in other forms, the anion; and in still other forms, the osmotic pressure of both ions comes into play. Where the osmotic pressure of the cation is the conditioning factor, we have this opposing the solution-tension of the metal, and what will occur depends upon the relative magnitudes of these two forces. Where the solution-tension of the metal is greater than the osmotic pressure of the cations, metal atoms separate from the bar, take a positive charge from it and pass into solution as cations, leaving the bar charged negatively.

When the osmotic pressure of the cations in the solution is greater, metal ions separate from the solution on to the bar, give up their positive charges to the bar, and the electrode is thus charged positively. This is the key to the action of the primary cell. The question that remains is this. Is the assumption of the solution-tension of the metals founded on fact? Is there any such force at the surface of contact of a metal and a solution say of one of its salts?

Experimental Proof of the Existence of Solution-Tension.— The fundamental point in connection with these deductions of Nernst is the existence of solution-tension. Can it be demonstrated? At first it was a *pure assumption.* Later, the existence of solution-tension was demonstrated by Palmaer,[1] in the following manner.

A vessel was filled with a solution of mercurous nitrate. Very finely divided mercury was allowed to rain down through the solution in the form of a mercury mist. Mercury is an element with a very low solution-tension, as we shall see. This means that when mercury comes in contact with a solution of one of its own salts, mercury ions separate from the solution on to the drop, charging it positively. As each positively charged droplet of mercury falls through the solution, it draws to it electrostatically the $\bar{N}O_3$ anions in the solution, and carries these down with it to the bottom of the vessel. At the bottom of the beaker is placed some mercury. When the positively charged falling drops come in contact with the mercury, the latter is also charged positively; the $\bar{N}O_3$ anions which were dragged down through the solution by the drop being set free at the surface of the mercury. The mercury at the bottom of the vessel now being charged positively, will throw mercury ions back again into the solution, and these cations will pair themselves off against the $\bar{N}O_3$ anions which now exist in large numbers just above the surface of the metal. The mercurous nitrate should thus become more concentrated just above the surface of the mercury, than in other parts of the solution.

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[1] *Zeit. phys. Chem.*, **25**, 265 (1898); **28**, 257 (1899).

This conclusion is based solely on the assumption of the existence of solution-tension of the metals. The facts confirm the conclusion. When the mercury is allowed to rain down in the form of a very fine mist, the mercurous nitrate just above the metallic mercury becomes as much as forty per cent more concentrated than the remainder of the solution.

By simply allowing finely divided mercury to rain down through a homogeneous solution of mercurous nitrate, and thus to change the concentration of the solution appreciably is a most surprising result. It could never have been suspected until we had the conception of the solution-tension of metals, and its existence is strong confirmation of the correctness of the assumption made by Nernst.

Values of the Solution-Tensions of Certain Metals.— It would lead us too far to discuss in any detail, in the present connection, the method of determining the solution-tension of the metals. For this reference must be had to some text-book[1] on Physical Chemistry. The results are of such importance and bear on so many problems that for some of the more common elements they are given in the following table.[1]

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[1] See Author's *Elements of Physical Chemistry*, 4th edition, p. 487. (The Macmillan Co.)

	Atmospheres
Magnesium	10^{44}
Zinc	10^{18}
Aluminium	10^{13}
Cadmium	10^{7}
Iron	10^{4}
Lead	10^{-3}
Mercury	10^{-16}
Silver	10^{-17}
Copper	10^{-20}

This tension-series, as it is called, tells us just which metals will precipitate other metals from solutions of their salts, when the metal is plunged into the solution. A metal in this tension-series will, in general, precipitate from solutions of its salts any metal which is lower down in the tension-series, and be precipitated from its own salts by a metal higher in the series. To secure this result, however, the metals should be sufficiently widely removed from one another in the series — there should be a sufficient difference in their solution-tensions. The best results are secured when a metal near the top of the series, like zinc, is plunged into the solution of a metal near the bottom of the series, like copper.

We are impressed by the enormous differences in the solution-tensions of the different metals. Thus, magnesium has a solution-tension of 10^{44} atmospheres, and copper, a solution-tension of only 10^{-20} atmospheres — a variation almost from infinite to infinitesimal.

At first thought, such extreme values are apt to impress one unfavorably. These metals show a general resemblance in other physical properties. Marked differences, to be sure, manifest themselves, but no differences of anything like the order of magnitude shown by the solution-tensions. Yet, when these experimentally found values are used in the equations for calculating the electromotive forces of primary cells containing these metals as electrodes, the calculated values are in agreement with those found experimentally to within the limit of error of experiment, and this is the real test of their worth.

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[1] Ostwald: *Lehrb. d. allg. Chem.*, II, 948 (1893).

We must accept, then, at least tentatively, the above values for the solution-tensions of the metals as corresponding to the facts of nature.

An interesting application of the solution-tension of the metals has been made by Ostwald[1] to explain why pure metals such as zinc do not dissolve in acids and why they do dissolve when platinum is brought in contact with them. He showed that zinc, being a metal with a high solution-tension, does not dissolve because the hydrogen ions of the acid cannot give up their charges to it and escape as hydrogen gas. When the zinc is attached to platinum — a metal with a low solution-tension — the hydrogen ions give up their charges to the platinum and escape as hydrogen gas, the zinc passing into solution.

Ostwald carried out this experiment in such a way as to illustrate also chemical action without mechanical contact. It would lead us too far to discuss this in detail here.[2] Suffice it to say that he showed that electrical contact rather than mechanical contact is essential in order that things may react chemically; mechanical contact being in general the simplest means of establishing electrical contact.

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[1] *Zeit. phys. Chem.*, **9**, 540 (1892).

[2] See *Elements of Physical Chemistry*, by the Author, 4th edition, p. 489. (The Macmillan Co.)

CHAPTER XI

SOLUTIONS IN NONAQUEOUS AND IN MIXED SOLVENTS

Solvent Power of Liquids. — The power of liquids to dissolve substances varies greatly from liquid to liquid. Of all known liquids water has the greatest solvent power, but we must not conclude that water has a monopoly, or anything approaching it, as a solvent. All liquids have some solvent power. Some liquids dissolve a large number of substances, and certain substances in large quantities. Thus, the alcohols, simple, or complex like glycerol, have very marked solvent power. The simple alcohols dissolve in large quantities many fats, oils, resins, and the like, which are either practically insoluble in water, or dissolve to only a very slight extent. Glycerol is an excellent solvent, especially at more elevated temperatures. Acetone dissolves a great variety of things, and the solutions in acetone have abnormal, and therefore very interesting properties; acetone having the power of polymerizing a great variety of substances when dissolved in it.

We also find good solvents among the inorganic liquids. Thus, liquid ammonia has very marked solvent power; liquid hydrocyanic acid is a good solvent for quite a variety of substances, and there are many other examples.

The Relative Powers of Different Liquids to Dissociate Electrolytes. — Let us consider first certain compounds of carbon. Take the simplest alcohols. The dissociating powers of these substances can now be measured by the improved conductivity method, and the power of methyl and ethyl alcohol to break molecules down into ions can also be measured by the improved boiling-point method,[1] as has already (p. 118) been seen. Methyl alcohol has from one-half to one-fourth the dissociating power of water; ethyl alcohol from one-third to one-fifth the dissociating power of water. The higher members of this series of alcohols, *i.e.*, those containing a larger number of carbon atoms, have *less and less dissociating power the more complex* the alcohol, and this is true in general of members of any homologous series of compounds of carbon. The more complex the compound, therefore, the higher it stands in the series, the less its power to break down molecules dissolved in it, into charged parts or ions.

For our knowledge of the dissociating powers of methyl and ethyl alcohols, we are indebted especially to the work of Carrara,[2] Zelinsky and Krapiwin,[3] Völlmer,[4] Kablukoff,[5] and Fitzpatrick.[6] Considerable work in the alcohols as solvents has also been done in this laboratory, as will appear especially in the later sections of this chapter, which deal with investigations in mixed solvents.

The work in the higher alcohols of this series we owe especially to Schlamp,[7] Carrara,[8] and Kablukoff.[9]

Schlamp showed that propyl alcohol has somewhat less than one-half the dissociating power of ethyl alcohol; thus illustrating the fact mentioned above, that the more complex the member of the homologous series the less its dissociating power.

The work of Kablukoff in isoamyl alcohol brought out a fact of interest and, no doubt, of importance, the meaning of which, however, is at present not understood. Hydrochloric acid dissolved in this solvent gave a molecular conductivity which *decreased with increase in dilution* (see p. 177). It will be recalled that this is exactly the reverse of the general effect of dilution on the molecular conductivity of solutions of electrolytes, the more dilute the solution the greater the molecular conductivity.

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[1] *Zeit. phys. Chem.*, **31**, 114 (1899).

[2] *Gazz. Chim. ital.*, **26**, I, 119 (1896).

[3] *Zeit. phys. Chem.*, **21**, 35 (1896).

[4] *Wied. Ann.*, **52**, 328 (1894).

[5] *Zeit. phys. Chem.*, **4**, 429 (1889).

[6] *Phil. Mag.*, **24**, 378 (1887).

[7] *Zeit. phys. Chem.*, **14**, 272 (1894).

[8] *Gazz. Chim. ital.*, **27**, I, 221 (1897).

[9] *Zeit. phys. Chem.*, **4**, 432 (1889).

Other Compounds of Carbon. — A similar relation was found by Kablukoff[1] in ether as a solvent. The molecular conductivity of hydrochloric acid in this solvent also decreases with the dilution. These same solutions were found to show less conductivity the higher the temperature to which they were heated — in a word, negative temperature coefficients of conductivity. This is true of metals in general, as we have seen, but is directly the opposite of what we find for nearly all solutions. The hydrocarbons, such as benzene, etc., have very little dissociating power. The same is true, in general, of the ethers, aldehydes, esters, and substitution products of these so-called neutral organic compounds.

Acetone has very pronounced dissociating power; indeed about one-fourth to one-fifth that of water. As already stated, solutions in acetone present a number of abnormal properties. Some of the molecules are largely associated and others are simultaneously broken down into ions. The best conductivity work in acetone we owe to St. v. Laszczynski,[2] Dutoit and Aston,[3] and Dutoit and Friderich.[4] Some work has been done in the more complex ketones, with the same general result, that the higher members of a homologous series have less dissociating power than the lower.

The conductivity of certain salts in pyridine was studied by Werner,[5] but most of the work on the dissociating power of this solvent we owe to St. v. Laszczynski and St. v. Gorski.[6] While the dissociating power of this solvent is not yet accurately known, still it is known to have very considerable power of breaking molecules down into ions.

There is one organic acid — formic acid — which was shown by the work of Zanniovich-Tessarin,[1] to have very great dissociating power. Indeed, the dissociating power of this solvent is of the same order of magnitude as that of water itself.

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[1] *Zeit. phys. Chem.*, **4**, 431 (1889).

[2] *Zeit. Elektrochem.*, **2**, 55 (1895).

[3] *Compt. rend.*, **125**, 240 (1897).

[4] *Bull. Soc. Chim.* [3], **19**, 321 (1898).

[5] *Zeit. anorg. Chem.*, **15**, I, 123 (1897).

[6] *Zeit. Elektrochem.*, **4**, 290 (1897).

The dissociating power of acetic acid was shown by Jones[2] to be very much less than that of formic acid.

The dissociating power of glycerol as a solvent has been studied at some length in the author's laboratory; but the results obtained will be discussed in a later section of this chapter, dealing primarily with mixed solvents.

The one to whom we probably owe more than to any other for our knowledge of the dissociating power of a large number of organic and inorganic solvents is Paul Walden[3] of Riga. He has studied the conductivities of electrolytes when dissolved in many unusual solvents, and has thrown light on the dissociating powers of many liquids. It would lead us too far to discuss these elaborate investigations here in any detail. A few points established by him are, however, of such interest and importance that they must be considered.

Solvents Other Than Carbon Compounds. — Walden showed that among the inorganic solvents some have very marked dissociating power, while others have scarcely any dissociating power at all. For example,[4] arsenic and antimony trichlorides and phosphorus oxychloride have marked dissociating power; while the trichloride and tribromide of phosphorus, the pentachloride of antimony, and stannic chloride have very little power to break molecules down into ions. Arsenic tribromide[5] also has considerable dissociating power. It is interesting to note the difference between the various halogen compounds of members of the phosphorus group, with respect to their power to break down molecules into ions.

[1] *Zeit. phys. Chem.*, **19,** 251 (1896).

[2] *Amer. Chem. Journ.*, **16,** 13 (1894).

[3] *Zeit. phys. Chem.*, **46,** 103 (1903); **54,** 129 (1906); **55,** 207, 281, 683 (1906).

[4] *Zeit. anorg. Chem.*, **25,** 209)1900).

[5] *Ibid.*, **29,** 371 (1902).

Abnormal Electrolytes. — One of the most striking relations brought out by Walden[1] deals with the so-called *abnormal electrolytes.* He found that when the halogens, phosphorus, arsenic, antimony, sulphur, and certain other substances were dissolved in such solvents as liquid sulphur dioxide and arsenic chloride, the solutions showed marked conductivity. How was this possible? The dissolved substances are elements, not electrolytes at all in the proper sense of the term. What kinds of ions do they yield? In order to conduct the current these substances must break down into both positively charged and negatively charged parts. We must have both cations and anions formed by these elementary substances. This is obviously different from the ordinary electrolytic dissociation of acids, bases and salts. Walden termed such substances in such solvents, abnormal electrolytes.

If we examine the work of Thomson[2] on the electrolysis of hydrogen gas, in which he showed that the molecule is made up of both positive and negative constituents, we will see a certain analogy between what takes place in the hydrogen when the current is passed through it, and what takes place when the above-named elements are dissolved in the different solvents. The hydrogen molecule is broken down into a positive and into a negative constituent, as is shown by the different spectra on the two sides of the metal septum.

It seems probable that the above elementary subtances are broken down by certain solvents into both positive and negative constituents or ions. Otherwise it would be difficult to see how such solutions could carry a current, and show conductivity as it is ordinarily measured.

Hydrocyanic Acid.— Centnerszwer[3] has shown that the dissociating power of liquid hydrocyanic acid, itself a compound of carbon, is greater even than that of water. This is very important as we shall see in connection with the relation between the dissociating powers of solvents and their other physical properties.

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[1] *Zeit. phys. Chem.*, **43**, 385 (1903).

[2] *Nature*, **52**, 451 (1895).

[3] *Zeit. phys. Chem.*, **39**, 217 (1902).

While liquid hydrocyanic acid has this remarkably high dissociating power, Centnerszwer has found that liquid cyanogen has very small dissociating power indeed. This is rather surprising when we consider that the only difference in chemical composition between these two compounds is an atom of hydrogen.

Hydrogen Dioxide. — Hydrogen dioxide has been shown by Jones[1] and his co-workers Barnes and Hyde, to have a higher dissociating power than water. This is not surprising when we consider the close relation chemically between hydrogen dioxide and water. The former is simply oxidized water. This fact is also of interest in connection with the relation just referred to between the dissociating power of liquids and certain of their other physical properties.

Dissociating Power of Liquid Ammonia. — Cady in 1897[2] discovered that solutions of salts in liquid ammonia are good conductors of the current. This led Franklin and Kraus[3] to take up an extensive study of the conductivity of salts dissolved in this solvent. They found that such solutions conducted far better than aqueous solutions of the same salts at the same concentrations. They at first concluded that such solutions are more dissociated than aqueous solutions of the same salts having the same concentrations. This conclusion was later somewhat modified. The conductivity of a solution is a function not only of the number of ions present, but also of the velocities with which they move. The velocities of the ions in liquid ammonia were shown to be much larger than in water, under the same conditions, as would be expected from the small viscosity of liquid ammonia.

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[1] *Amer. Chem. Journ.*, **27**, 22 (1902).

[2] *Journ. Phys. Chem.*, **1**, 707 (1897).

[3] *Amer. Chem. Journ.*, **20**, 820, 836 (1898); **21**, 8 (1899); **23**, 277 (1900); **24**, 83 (1900); **28**, 83 (1902); *Journ. Amer. Chem. Soc.*, **26**, 499 (1904); **27**, 191 (1905); **29**, 1389 (1907).

When this was taken into account, it was found that salts dissolved in liquid ammonia are dissociated to about one-fourth the extent that they are in water under the same conditions.

Lewis[1] carried out an investigation in iodine as the solvent. He found that in dilute solutions the conductivity of potassium iodide dissolved in this solvent increases rapidly with concentration up to a maximum, after which it falls off. This would lead one to suspect that there is some compound formed between the solvent and the dissolved substance.

In connection with the work in nonaqueous solvents, we should mention that of Archibald and McIntosh, who used as solvents the liquefied halogen acids, hydrochloric, hydrobromic, and hydriodic, and also liquid hydrogen sulphide. Organic compounds dissolved in these solvents showed an increase in the molecular conductivity with increase in the concentration of the solution. They pointed out that there are a fairly large number of examples illustrating this same condition, the number being much larger than any one supposed before they were thus collected.

Davis and Putnam,[2] working in this laboratory, have made a fairly extensive study of the conductivity of solutions of salts in formamide as the solvent. They have found that formamide has a greater dissociating power than water; salts being completely dissociated in it at lower dilutions than in water. This again is interesting in connection with a certain relation between dissociating power and another property, which will soon be discussed.

The dissociating power of the different solvents is not simply a function of the nature of the solvents, but depends also on the nature of the dissolved substance. This has long been known, and is shown very clearly by work on the organic acids in alcohol, which has been carried out in this laboratory during the past two years. Wightman and Wiesel[1] found that the conductivity of organic acids in ethyl alcohol are very small indeed; being in general several hundred times less than in water at the same concentration of the solutions. This was confirmed by the work of Lloyd and Wiesel[2] in which the conductivity of about forty organic acids in ethyl alcohol, over a considerable range of dilution, was studied.

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[1] *Zeit. phys. Chem.*, **56**, 179 (1906).

[2] *Carnegie Institution of Washington*, Publication No. 230, Chap. II (1915).

Dissociating Power of Solvents and Their Dielectric Constant. — A relation of importance was pointed out first by Thomson,[3] and a little later but independently by Nernst,[4] between the dissociating power of solvents and their dielectric constants. A word as to what is meant by the dielectric constant of a medium. It is the same property of media that was called by Faraday their "specific inductive capacity." The numerical value of this constant for any medium determines the force of attraction between opposite electrical charges separated by the medium in question. Indeed, the dielectric constant has been defined as the relation between the force exerted between two charged bodies in a vacuum and when separated by the medium in question. This can be seen at once if we consider the law governing such phenomena — the law of Coulomb.

Suppose we have two electrical charges which we will call l_1 and l_2 at a distance apart r, the force of attraction or repulsion, f, between them will be expressed by the equation:

$$f = \frac{l_1 l_2}{r^2} \frac{1}{K}$$

in which K is the dielectric constant of the medium separating the two charges.

We see at once that K being in the denominator, the larger its value the smaller the electrostatic force acting between the charges, — the force is inversely proportional to K.

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[1] *Journ. Amer. Chem. Soc.*, **36**, 2243 (1914).

[2] *Carnegie Institution of Washington*, Publication No. 230, Chap. VII (1915).

[3] *Phil. Mag.*, **36**, 320 (1893).

[4] *Zeit. phys. Chem.*, **13**, 531 (1894).

Why should there be any relation between the dielectric constants of media and their own power to dissociate molecules dissolved in them? The author has been best able to form a picture of this relation in the following manner. Take for example, a solvent like water, which has a large dielectric constant. The force of attraction between the positively charged cation, and the negatively charged anion, of the electrolyte dissolved in the water, is inversely proportional to the dielectric constant of the solvent. This being large in the case of water, the force of attraction between the positively and negatively charged parts is small. There being but a small force to hold the cation and the anion together in the molecule, they separate or undergo electrolytic dissociation readily.

If the dielectric constant of the medium is small, as in the case of the hydrocarbons, the force of attraction between the oppositely charged parts is large, and they do not separate or undergo electrolytic dissociation to any appreciable extent.

Determination of the Dielectric Constants of Media. — It is unsatisfactory to deal with any quantity and not have some idea how it is measured. A number of methods have been proposed and used for determining the dielectric constants of liquids. All things considered, probably the best of these is the method of Drude.[1] It consists in passing electrical waves down two parallel wires surrounded by the medium in question, and measuring the length of the waves. The wave-length is inversely proportional to the square root of K, or the dielectric constant of the medium. The following table contains the dielectric constants of a number of liquids, many of which are good solvents, and also their approximate relative dissociating powers.

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[1] *Zeit. phys. Chem.*, **23**, 267 (1897).

Solvent	Dielectric constant	Dissociating power
Hydrocyanic acid	95	greater than water
Hydrogen dioxide	93	greater than water
Formamide	84	greater than water
Water	81.7	1
Formic acid	62.0	less than water
Methyl alcohol	35.3	about $\frac{1}{2}$
Ethyl alcohol	26.0	about $\frac{1}{3}$
Ammonia	22.0	about $\frac{1}{4}$
Acetone	20.7	about $\frac{1}{4}$
Glycerol	16.5	$\frac{1}{2}$
Ethyl ether	43.7	small
Benzene	2.4	very small
Toluene	2.4	very small

That the relation in question obtains, at least, approximately is shown by the above results.

Relation Between the Dissociating Power of Solvents and Their Own Association. — A relation between the dissociating power of solvents and another property of these liquids was pointed out by Dutoit and Aston,[1] which, while it does not hold rigidly, undoubtedly contains much of value. The relation in question is between the dissociating power of solvents and their own association; and this raises the question, how are we to determine the degree of association of any substance in the liquid state? This has been done by several independent methods, which it would lead us too far to discuss here in any detail. One of these is the method of Ramsay and Shields,[2] based upon measurements of the surface-tension of liquids, and which has a good physical foundation. Another is the purely empirical method of Longinescu,[3] which consists in determining the densities and boiling-points of liquids. A third method has been suggested by Guye,[4] which is based upon the measurement of the refractivity of liquids under certain special conditions.[5]

The significance of this relation can be seen by comparing the association factors for a number of liquids, at a given temperature, with the dissociating powers of these liquids acting as solvents.

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[1] *Compt. Rend.*, **125**, 240 (1897).

[2] *Zeit. phys. Chem.*, **12**, 433 (1893).

[3] *Journ. Chim. Phys.*, **1**, 289 (1903).

[4] *Ann. Chim. Phys.* [6], **21**, 211 (1890).

[5] For details see *Elements of Physical Chemistry*, by the author, 4th edition, p. 145. (The Macmillan Co.)

Solvent	Association factor	Dissociating power
Formamide	6.2	greater than water
Water	3.8	1
Methyl alcohol	3.4	about ½
Ethyl alcohol	2.7	about ⅓
Glycerol	1.8	about ½
Acetone	1.3	about ¼

In making this comparison we are limited to those liquids of which the association factors have been ascertained.

This relation between the dissociating power of solvents and their own association is not a quantitative one, as has already been pointed out; but it is rather more than qualitative. Other things being equal, those solvents which are the most associated have the greatest dissociating power. It might also be pointed out in passing that many of the best solvents are strongly associated compounds.

Effect of Rise in Temperature on the Association of Liquids and on Their Dissociating Power. — When we were studying the dissociation of electrolytes as measured by conductivity, it was pointed out that rise in temperature diminishes the dissociation of a solution of an electrolyte. This raises the question, what is the effect of rise in temperature on the association of liquids?

It is well known that rise in temperature tends to break down complexes in general; and this has been shown to be the case with associated molecules. The association of liquids over a wide range in temperature, extending from ordinary temperatures almost to the critical temperature of the liquid in question, was measured by Ramsay and Shields, with the result that the *higher the temperature the less the liquid is associated.* This is, then, another relation between the association of liquids and their power to break down molecules into ions.

Results in Mixed Solvents. — A fairly large amount of work has been done, especially in this laboratory, on the condition of substances in mixtures of solvents.

The observation was made by Zelinsky and Krapiwin,[1] that certain salts when dissolved in a certain mixture of methyl alcohol and water, showed *lower conductivities than when dissolved in pure methyl alcohol*; notwithstanding the fact that the same salts, under the same condition of dilution, showed much lower conductivity in methyl alcohol than in water. This was indeed a remarkable fact, and merited careful and extensive investigation. The following discussion is taken from Publication of the Carnegie Institution of Washington, No. 210, pp. 162–170.[2]

Mixtures of Water and the Alcohols. — The study of the conductivities and dissociations in pure solvents was extended in this laboratory to mixed solvents, and the results have been published in monographs Nos. 80 and 180 of the Carnegie Institution of Washington.

The first investigation was carried out by Lindsay[3] who worked in water, in methyl, ethyl, and propyl alcohols, and in mixtures of these solvents with one another. He found that in certain mixtures of the alcohols with water, the conductivity of the dissolved salt was less than in the pure alcohol. The conductivity curves in mixtures of methyl alcohol and water showed very distinct minima, and a conductivity minimum was also frequently found in mixtures of ethyl alcohol and water.

A possible explanation of the results in mixtures of the alcohols with water is that each solvent diminishes the association of the other. Since the dissociating power of a solvent is in general greater the larger its own association, it follows that whatever would decrease the association of a liquid would decrease its power to dissociate electrolytes dissolved in it. The question is, does one associated liquid diminish the association of another associated liquid?

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[1] *Zeit. phys. Chem.*, **21**, 35 (1896).

[2] See also *Journal of the Franklin Institute,* Nov. and Dec., 1913.

[3] *Amer. Chem. Journ.*, **28**, 329 (1902).

An associated liquid tears down the molecules of an electrolyte dissolved in it into simpler parts or ions; and it might be expected that such a liquid would tear down the molecules of another associated liquid, a non-electrolyte, not into charged parts or ions, but into simpler molecules. Alcohol and water are associated liquids, as has been shown by the surface-tension measurements of Ramsay and Shields.[1] Do these diminish the association of one another?

That this is the case was shown by Murray.[2] He worked with the associated liquids, water, formic acid, and acetic acid. He determined the molecular weight of each of these liquids in the other two, and found that their molecular weights became smaller the more dilute the solutions. This showed that the solvent, *i.e.*, the liquid present in the larger quantity, was tearing down the molecular complexes of the dissolved liquid or the one present in smaller quantity.

That there is a diminution in the association of one associated liquid by another associated liquid was shown for the above-named substances and made highly probable for others.

That this was not the entire explanation of the nature of the conductivity curves in mixtures of certain alcohols with water, was brought out by the next investigation in this field, carried out by Carroll.[3] He compared the conductivity curves of electrolytes dissolved in these solvents with the fluidity curves of the mixtures of the two liquids in question, and found that the two sets of curves were very similar. The minima in the two cases occurred in the same mixture of the two liquids. A careful comparison of the two sets of phenomena led us to conclude that the conductivity maxima are largely due to the decrease in fluidity which takes place on mixing the two solvents. The diminished fluidity, or increased viscosity, would cause the ions to move more slowly, and hence decrease the conductivity.

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[1] *Zeit. phys. Chem.*, **12**, 433 (1893).

[2] *Amer. Chem. Jour.*, **30**, 193 (1903).

[3] *Ibid.*, **32**, 521 (1904).

At the end of the work done by Carroll, it seemed justifiable to conclude that the conductivities of binary electrolytes in such solvents as those already considered, are inversely proportional to the coefficients of viscosity of the solvent and are directly proportional to the association of the solvent. Bassett[1] showed that silver nitrate in mixtures of methyl alcohol and water gave a conductivity minimum at both 0° and 25°; also that the effect of one solvent on the other was greater at 0° than at 25°. This would be expected, since the dissociation diminishes with rise in temperature, and each solvent would probably diminish the association of the other less, the smaller its own association or the higher its temperature.

Mixtures of Acetone with Water and the Alcohols. — Bingham[2] measured not only the conductivities, but also the viscosities of a number of solvents and solutions in these solvents. He found minima in the conductivity curves in mixtures of acetone and water. The distinctly new feature brought out by the work of Bingham was that lithium and calcium nitrates in mixtures of acetone with methyl and ethyl alcohols showed a decided maximum in the conductivity curves. This must be due either to an increase in dissociation in such mixtures, increasing the number of ions present, and consequently increasing the conductivity, or it must be due to a diminution in the complexity of the solvates around the ions, increasing their velocities. The dissociation was measured in the mixtures in question and found not to account for the phenomenon. This eliminates increase in dissociation and leaves the other alternative, diminution in the complexity of the solvate, to account for the phenomenon.

The ion must take with it through the solvent any molecules of the liquid with which it might be combined. This would increase the effective mass and diminish its velocity. Anything which would diminish the complexity of the solvate about the ion would increase its velocity, and consequently the conductivity. We must therefore conclude that the solvates in those mixtures of acetone with the alcohols are simplest where the conductivity is the greatest.

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[1] *Amer. Chem. Journ.*, **32**, 409 (1904).

[2] *Ibid.*, **34**, 481 (1905).

Rouiller[1] studied both the velocities of the ions and the conductivities of electrolytes in mixtures of acetone with the alcohols. Silver nitrate in methyl alcohol and acetone gave a decided maximum of conductivity. His work on the velocities of the ions in these mixtures indicated that the above explanation of the maxima offered by Jones and Bingham was correct; there is a change in the complexity of the solvate about the ion.

McMaster[2] extended the work in the same solvents — water, methyl alcohol, ethyl alcohol, and acetone — and in mixtures of these with each other. He found conductivity results of the same general character as those obtained by the earlier workers. Conductivity minima were found in mixtures of the alcohols with water and acetone with water. Conductivity maxima were obtained with lithium bromide in mixtures of methyl or ethyl alcohol with acetone. Cobalt chloride in mixtures of acetone with ethyl alcohol also showed a maximum. Jones and McMaster reached the same conclusion from their work that had been reached by Jones and Bingham. Change in the complexity of the solvate formed by the ion in different mixtures of solvents is an important factor in determining the conductivity maxima.

A point of interest brought out by the work of McMaster is in connection with the temperature coefficients of conductivity in non-aqueous solutions. The bearing of temperature coefficients of conductivity on the solvate theory of solution has already been discussed. With rise in temperature the hydrates about the ions become simpler. The mass and probably the size of the ion thus becomes less, and it moves faster the higher the temperature, thus increasing the conductivity.

McMaster found that cobalt chloride in certain mixtures of acetone with the alcohols showed, at ordinary temperatures, negative temperature coefficients of conductivity. What does this mean? The solvent becomes less viscous with rise in temperature, thus increasing the velocity of the ions; and the solvates become simpler, which also increases the velocity with which the ions move.

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[1] *Amer. Chem. Journ.*, **36**, 427 (1906).

[2] *Ibid.*, **36**, 325 (1906).

With rise in temperature, on the other hand, the association of the solvent, and consequently its dissociating power, becomes less.

The above two influences work counter to one another. Negative temperature coefficients of conductivity mean that the latter influence predominates. The alcohols used and acetone are highly associated liquids. Rise in temperature diminishes their association and consequently their dissociating power.

A solution of cobalt chloride in a 75 per cent mixture of acetone with methyl alcohol, the solution being $\frac{1}{200}$ normal, had a zero temperature coefficient of conductivity.

Viscosity and Atomic Volume. — A number of points of interest were brought out by the next investigator, Veazey.[1] He worked with solutions of salts in water, methyl alcohol, ethyl alcohol, acetone, and in binary mixtures of these liquids with one another. The minimum in conductivity was found to be a more general phenomenon than had been supposed from the earlier work. It had long been known that mixtures of methyl alcohol and water or ethyl alcohol and water, are more viscous than either of the pure solvents alone. A rational explanation of this phenomenon was suggested — alcohol and water are strongly associated liquids. When two associated liquids are mixed each diminishes the association of the other. The larger molecules are thus broken down into smaller molecules, which increases the frictional surfaces when these molecules move over one another as they do in viscous flow. The result would be to increase the viscosity of the mixture over that of either pure solvent.

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[1] *Amer. Chem. Journ.*, **37**, 405 (1907). *Zeit. phys. Chem.*, **61**, 641 (1908); **62**, 44 (1908).

Maxima in the conductivity of electrolytes in the mixed solvents were shown to correspond to maxima in the fluidity of the mixed solvents. Maxima in fluidity are probably due to an increase in the size of the molecules of the solvent, due to a combination of one liquid with the other. This would diminish the viscosity and consequently increase the velocity of the ions, which would increase the conductivity. This factor must also be taken into account in explaining conductivity maxima.

The temperature coefficients of conductivity in the above-named mixtures of liquids with water are a maximum in the 25 and 50 per cent mixtures. These are just about the mixtures in which the solvents have the least association. The molecules of the solvent being in the simplest condition would be most favorable for chemical action. In such mixtures the solvents probably combine to the greatest extent with the dissolved substance — the solvation is at a maximum. The effect of rise in temperature breaking down these solvates would therefore be a maximum where solvation is a maximum. Solutions of potassium sulphocyanate have greater conductivity in acetone than in water. This was shown to be due to the greater fluidity of the acetone.

This same salt when dissolved in water lowers the viscosity of the water. Certain salts of potassium and salts of rubidium and caesium were practically the only ones known at that to lower the viscosity of water. In the case of certain salts of potassium the positive effect of the anion on the viscosity of water may more than offset the negative effect of the potassium ion.

The following explanation of the above-named phenomenon was suggested. If the atomic volume of the ions dissolved in the solvent were larger than the molecular volume of the solvent, the larger ions would diminish the size of the frictional surfaces coming in contact and would lower the viscosity.

It is well known that potassium, rubidium, and caesium occupy the maxima on the atomic-volume curve, and have much larger atomic volumes than any other known elements. Potassium has a smaller atomic volume than rubidium, and rubidium than caesium. Potassium chloride lowers the viscosity of water less than rubidium chloride, and rubidium chloride less than caesium chloride.

If we study the salts which raise the viscosity of water, we will find, in general, that the amount of increase in the viscosity bears a relation to the atomic or ionic volumes of the dissolved substances. Smaller ions tend to increase the viscosity of water more than larger ones. It would therefore seem that the above explanation contains a large element of truth.

Dissociation in Nonaqueous Solvents. — The problem of measuring dissociation in nonaqueous solvents is a difficult one. The freezing-point method is frequently not applicable. Many common solvents, such as the alcohols, freeze at temperatures which are too widely removed from the ordinary temperature of the laboratory to be measured with sufficient accuracy. The boiling-point method could be used only with fairly concentrated solutions. Dilute solutions produce such a slight rise in the boiling-point that this small quantity cannot be measured with a very high degree of accuracy. The boiling-point method has the further disadvantage of being so largely affected by slight changes in the barometer.

The hope of measuring dissociation in nonaqueous solvents in general seemed to rest in the conductivity method. This method as ordinarily applied would not be satisfactory. The dilution at which complete dissociation would be reached in such solvents is so great that the Kohlrausch method in any such form as he left it could not be applied to the problem.

The conductivity method was greatly improved by Kreider[1]; the greatest improvement being in the form of cell employed. With the improved method Kreider studied the dissociations of a number of salts in methyl and ethyl alcohols and in mixtures of these solvents with water. He measured the conductivities of solutions as dilute as 100,000 liters and found the following relation to hold:

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[1] *Amer. Chem. Journ.*, **45**, 282 (1911).

$$\frac{\mu_\infty \text{ methyl alcohol}}{\mu_\infty \text{ ethyl alcohol}} = \text{constant}.$$

When a salt is equally dissociated by each of two solvents, for the same concentration of the salt there is the same number of ions in the two solutions. Conductivity is a function of the number of the ions and their velocities. When the number of the ions is constant, as in this case, conductivity is a function of the relative velocities of the ions. The velocity of an ion is conditioned by its mass and volume and by the fluidity of the solvent. If the mass and volume of the ions in the two solvents are constant, the velocities of the ions should vary as the fluidities of the solvents. The ratio between the values of μ_∞ in the two solvents should be the same as the ratio between the fluidities of these solvents. This was, however, found not to be the case. The bearing of this fact on the condition of the ions in the two solvents in question is important. This shows that the mass and probably the volume of the solvated ion must differ in the two solvents.

The ratio between the values of μ_∞ for a salt in the two solvents, compared with the ratio between the fluidities of the two solvents, would give an approximate idea of the relative solvation of the ions in the two solvents in question.

This method will be still further applied to the problem of solvation in non-aqueous solvents.

Ternary Mixtures of the Alcohols with Water. — Mahin[1] studied electrolytes in ternary mixtures of the alcohols with water, and obtained results of the same general character as those found in binary mixtures of these solvents. He then took up work in binary mixtures, one constituent being acetone. Acetone was studied primarily because in many of its properties it is an exceptional solvent. Substances dissolved in acetone are largely polymerized, and acetone has at the same time considerable dissociating power. Furthermore, acetone is a solvent with small viscosity, and it was desired to see whether the relations found for solvents with larger viscosity would hold here. The curve for conductivity and for fluidity were worked out and the two compared.

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[1] *Amer. Chem. Journ.*, **41**, 433 (1909); *Zeit. phys. Chem.*, **69**, 389 (1909).

It was found that the product of molecular conductivity and viscosity is nearly a constant at complete dissociation. This means that for completely dissociated solutions in acetone the curves of molecular conductivity are similar to those of fluidity — conductivity being inversely proportional to viscosity. This relation is of interest in that it holds in a solvent with such small viscosity as acetone.

Relations such as those referred to above having been found to hold in a solvent with such small viscosity as acetone, the question arose, do such relations obtain in a highly viscous solvent like glycerol? Glycerol not only has a very high viscosity, but is an excellent solvent, and has a large dielectric constant, which means that it has considerable dissociating power. Glycerol is somewhat strongly associated, which also indicates considerable dissociating power.

Glycerol and Mixtures with the Alcohols and Water. — The first investigation in glycerol as a solvent was carried out by Schmidt.[1] He measured the conductivities of solutions of certain salts in glycerol, and in mixtures of glycerol with water and with methyl and ethyl alcohols. The conductivities were measured at different temperatures. The most striking relation noted was the enormous magnitude of the temperature coefficients of conductivity of electrolytes dissolved in glycerol. This was shown to be due to the rapid decrease in the viscosity of glycerol with rise in temperature.

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[1] *Amer. Chem. Journ.*, **42**, 37 (1909).

It was shown that when glycerol is mixed with water or the alcohols, there is a breaking down of the association of each solvent by the other, and a consequent diminution in the dissociating power. Solutions of potassium iodide in 25 and 50 per cent mixtures of glycerol and water were less viscous than the solvents themselves. This salt does not lower the viscosity of glycerol, but of the mixtures. The meaning of negative viscosity effects was discussed in the work of Veazey. While Schmidt did not study any salt which lowers the viscosity of pure glycerol, he found that the effect of the salt on the viscosity of pure glycerol was inversely as the molecular volume or atomic volumes of the constituents of the salt. This was in keeping with the explanation offered by Jones and Veazey to account for the changes in the viscosity of the solvent by the dissolved substance. A comparison of the conductivity and fluidity curves shows that the two run nearly parallel. Although glycerol has about 1,000 times the viscosity of methyl alcohol, yet, from the work of Schmidt, the same general relations obtain here that hold for the far less viscous solvents.

The work of Schmidt was continued by Guy.[1] He worked with a much larger number of salts, and over the temperature range 25° to 75°. He studied not only solutions in glycerol, but in mixtures of glycerol with water, with methyl, and with ethyl alcohols.

Guy found also enormous temperature coefficients of conductivity. This may be due to either of two causes: a change in dissociation with rise in temperature, or a change in the velocity of the ions. We know the order of magnitude of the change in dissociation with rise in temperature, and it is small. The chief cause of the large temperature coefficients of conductivity in glycerol is, then, an increase in the velocities with which the ions move. As we have seen, this may be due to a decrease in the viscosity of the solvent with rise in temperature, or may be caused by a breaking down of complex solvates about the ions.

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[1] *Amer. Chem. Journ.*, **46**, 131 (1911).

While the viscosity of glycerol decreases rapidly with rise in temperature, this alone would not account for the magnitude of the temperature coefficients of conductivity of glycerol solutions. There seems to be good evidence for the formation of glycerolates in solutions in glycerol. The temperature coefficients of conductivity in glycerol are greater at high than at low dilution. Jones has pointed out that this would be expected from the solvate theory. The more dilute the solution the more complex the solvate; the more complex the solvate the greater the change in its complexity with rise in temperature.

Further, salts of calcium, strontium, and barium have larger temperature coefficients of conductivity than those of sodium, potassium, and ammonium. The former are strongly hydrated, the latter weakly hydrated substances. It would seem that the former are more strongly glycerolated than the latter. Salts which have approximately the same hydrating power have temperature coefficients of conductivity in glycerol of the same order of magnitude, indicating the same order of magnitude of glycerolation. Work in the mixed solvents indicates that water diminishes the association of glycerol.

Solutions of salts in glycerol have in general greater viscosity than pure glycerol. Guy, however, found marked exceptions to this relation. Salts of rubidium lowered the viscosity of glycerol. Ammonium bromide and iodide also lowered the viscosity of this solvent. That rubidium should lower the viscosity of glycerol is in keeping with what was found in aqueous solutions. Salts of rubidium and caesium and some salts of potassium lowered the viscosity of water. This has already been explained as due to the large atomic volumes of these elements. The same explanation holds for solutions in glycerol.

Davis[1] continued the work of Guy, studying especially the effect of salts on the viscosity of glycerol. He repeated the work with ammonium iodide and obtained the same result that had been earlier found by Guy. He studied rubidium chloride, bromide, iodide, and nitrate, and showed that these lowered the viscosity of glycerol. The rubidium salts lower the viscosity of glycerol to such an extent that they appreciably increase their own conductivity in this solvent.

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[1] *Zeit. phys. Chem.*, **81,** 68 (1912).

Comparing the effects of the chloride, bromide, and iodide of rubidium on the viscosity of glycerol, Davis found that the chloride has the least effect, the bromide next, the iodide the greatest. He showed that this was in the same order as the molecular volumes of the salts in question. The results obtained with glycerol were, then, analogous to those obtained with water, both with respect to viscosity and solution.

Rubidium Salts in Mixtures of Acetone and Water. — Davis and Hughes[1] studied the conductivities and viscosities of solutions of rubidium salts in mixtures of acetone and water, from the standpoint of the theory of viscosity proposed by Jones and Veazey. They found that the viscosities of the mixture were lowered when it did not contain an excess of acetone; the effect, however, being less than in water or in glycerol.

Work in Formamide. — Davis and Putnam[2] studied the viscosities of solutions in formamide as a solvent. This was of interest in that formamide has a higher dielectric constant than water, and would therefore be expected to have greater dissociating power. Further, it is a very strongly associated solvent, being more associated than water, and this also would indicate greater dissociating power.

A specially devised apparatus for distilling under diminished pressure enabled the investigators to prepare formamide with a conductivity comparable with that of conductivity water. They showed that this solvent has greater dissociating power than water, and that those salts which form hydrates with water are solvated also in formamide.

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[1] *Zeit. phys. Chem.*, **85**, 513 (1913).

[2] *Carnegie Institution of Washington*, Publication No. **230**, Chap. II (1915).

The temperature coefficients of conductivity in formamide are what would be expected from the coefficients of hydrated salts in aqueous solutions.

Viscosities of Caesium Salts. — Having obtained a liberal supply of a caesium salt through the co-operation of Professor Howe of Washington and Lee University, Davis[1] was able to study the effect of caesium salts on the viscosity of water and other solvents. Caesium, as is well known, occupies the highest maximum on the atomic volume curve, having the largest atomic volume of all the elements. In terms of the theory proposed by Jones and Veazey, caesium salts should lower the viscosity of solvents even more than salts of rubidium, and such is the fact.

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[1] *Carnegie Institution of Washington*, Publication No. **230,** Chap. I (1915).

CHAPTER XII

COLLOIDAL SOLUTIONS

Historical Sketch. — There are few phases of solution which have recently attracted so much attention as colloids. We hear continually of colloidal solutions and of the remarkable properties possessed by matter in the colloidal state.

While this subject has come to the front only in the last few years, matter in the colloidal state has been known for over half a century. The Italian chemist Selmi, as early as 1844, recognized the difference between true solutions and apparent solutions of such substances as sulphur, Berlin blue, and the like. He called the latter pseudo-solutions, and recognized certain fundamental differences between these and true solutions. He pointed out that when pseudo-solutions are formed no change in temperature is produced. Further, there is neither contraction nor expansion of the liquid, and when salts are added, the colloid is precipitated. He observed that in such precipitations, a part of the precipitant is carried down with the colloid.

Selmi assumed that in pseudo-solutions the substance was in the state of an *emulsion* or a *suspension*.

Work of Graham. — The first to study colloids extensively was the English chemist, Graham. He found that those compounds which readily form crystals, diffuse rapidly through membranes made of vegetable parchment; while non-crystallizable or amorphous substances either do not diffuse at all through such membranes, or diffuse very slowly through them. The former Graham called *crystalloids*, and the latter, *colloids*. He used diffusion for separating the one class from the other — crystalloids from colloids — and likened these separations by diffusion to the separations based upon the different volatility of substances.

Graham saw the importance of colloids not only for inanimate, but for living matter. This can be seen best by quoting his own words.[1] "The colloidal is, in fact, a dynamical state of matter; the crystalloidal being the statical condition. The colloid possesses *energia*. It may be looked upon as the probable primary source of the force appearing in the phenomena of vitality. To the gradual manner in which colloidal changes take place (for they always demand time as an element), may the characteristic protraction of chemical-organic changes also be referred."

This is prophetic of what is now supposed to be the importance of colloids for the life process, and for the normal functions of living matter.

Diffusion Experiments of Graham. — Graham carried out his diffusion experiments with comparatively crude apparatus. The bottom of a wide glass cylinder or dish was covered with vegetable parchment, and this was floated on water. The substance was placed in the vessel and separated from the water by the membrane. The crystalloids passed through the membrane, and the colloids either did not pass through at all, or passed through only very slowly.

A few of the results obtained by Graham will give an idea of the relative rates at which crystalloids and colloids diffuse. Representing as unity the amount of sodium chloride which diffuses through the parchment paper in twenty-four hours at 10° to 15°, Graham[2] found that the relative rates at which other substances will diffuse are those given in the following table.

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[1] *Phil. Trans.*, **151,** 184 (1861).

[2] *Ibid.*, 203 (1861).

	Relative rates of diffusion
Sodium chloride	1.0
Alcohol	0.476
Glycerol	0.440
Mannite	0.349
Milk-sugar	0.185
Cane-sugar	0.214
Gum arabic	0.004

These data show the almost non-diffusability of colloids as compared with crystalloids.

The separation of crystalloids from colloids by diffusion Graham termed *dialysis*, and the apparatus for effecting such separations a *dialyzer*. This is one of the most efficient methods of freeing colloids from crystalloids. The mixture is placed in a dialyzer, when the crystalloid passes through and the colloid remains behind. We shall see, however, that this method of separating crystalloids from colloids is often far from quantitative. When colloids are precipitated by the addition of crystalloids, as is often done, the colloid frequently carries down some of the crystalloid with it, and holds it so firmly that it will not diffuse out and leave the pure colloid behind. Frequently, in such cases, the colloid cannot be washed free from the crystalloid.

This method based upon dialysis is, however, a fairly general method for obtaining colloids reasonably free from crystalloid impurities.

Graham gives a number of examples of colloids prepared by dialysis. Thus, neutral aluminium chloride dialyzes without undergoing any decomposition. When hydrated alumina is dissolved in aluminium chloride and the mixture dialyzed, there remains behind soluble hydrated alumina. After standing in the dialyzer for nearly a month this was found to contain only a trace of hydrochloric acid. Graham points out that soluble alumina is very unstable, being precipitated by a mere trace of almost any salt or acid. He obtained similar results with chromium hydroxide.

Graham prepared organic as well as inorganic colloids by dialysis. Thus, caramel and albumen were obtained in the form of colloidal solutions.

Graham's Views on Colloids. — Near the close of his great paper, Graham[1] summarizes his views on colloids. What these were can be seen best by quoting his own words, at least in part.

"I may be allowed to advert again to the radical distinction assumed in this paper to exist between colloids and crystalloids in their intimate molecular constitution. Every physical and chemical property is characteristically modified in each class. They appear like different worlds of matter, and give occasion to a corresponding division of chemical science. The distinction between these kinds of matter is that subsisting between the material of a mineral and the material of an organized mass."

Again,[2] "The phenomena of the solution of a salt or crystalloid probably all appear in the solution of a colloid, but greatly reduced in degree. The process becomes slow; time, indeed, appearing essential to all colloidal changes. The change of temperature, usually occurring in the act of solution, becomes barely perceptible." . . . "The colloid, although often dissolved in a large proportion by its solvent, is held in solution by a singularly feeble force. Hence colloids are generally displaced and precipitated by the addition to their solution of any substance from the other class. Of all the properties of liquid colloids, their slow diffusion in water, and their arrest by colloidal septa, are the most serviceable in distinguishing them from crystalloids. Colloids have feeble chemical reactions." "It[3] is difficult to avoid associating the inertness of colloids with their high equivalents, particularly where the high number appears to be attained by the repetition of a smaller number. The inquiry suggests itself whether the colloid molecule may not be constituted by the grouping together of a number of smaller crystalloid molecules, and whether the basis of colloidality may not really be this composite character of the molecule."

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[1] *Phil. Trans.*, **151**, 220 (1861).

[2] *Ibid.*, 220 (1861).

[3] *Ibid.*, 221 (1861).

This remarkable paper concludes with a discussion of "Osmose,"[1] which contains essentially the views that we hold today. "It now appears to me that the water movement in osmose is an affair of hydration and of dehydration in the substance of the membrane or other colloid septum. The outer surface of the membrane being in contact with pure water tends to hydrate itself to a higher degree than the inner surface does, the latter surface being supposed to be in contact with a saline solution." Where the membrane comes in contact with the solution, "the degree of hydration is lowered, and the water must be given up by the inner layer of the membrane and it forms the osmose."

This is essentially the view we hold today in connection with the passage of water through semipermeable colloidal membranes in the measurement of osmotic pressure.

A brief reference has, then, been made to some of the experimental work of Graham on colloids; and to some of his more important conclusions in regard to this state of matter. All things considered, we must regard this distinguished English chemist as the father of colloidal chemistry.

Work of M. Carey Lea. — The American chemist M. Carey Lea[2] in 1889 made a discovery which attracted considerable attention. He reduced a ten percent solution of silver nitrate with a solution of ferrous sulphate, to which a solution of sodium citrate and sodium carbonate was added. The precipitated silver was soluble and he thus obtained a solution which contained more than 95 percent of silver, and such systems were called by him solutions of metallic silver.

Although Loew[3] in 1883, and Muthmann[4] in 1887, had prepared colloidal solutions of silver, their work at that time had not aroused any very great interest. Lea regarded his preparation as a true solution of metallic silver, or an allotropic modification of silver. When it is recalled that silver is one of the most insoluble metals in water, and here was apparently a solution containing more than 95 percent of silver, we can see the reason for the strong impression, not to say sensation, created by the discovery of M. Carey Lea.

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[1] *Phil. Trans.*, **151**, 223 (1861).

[2] *Amer. Journ. Sci.*, **37**, 476 (1889); **38**, 47, 237, 241 (1889).

[3] *Ber. d. chem. Gesell.*, **16**, 2707 (1883).

[4] *Ibid.*, **20**, 983 (1887).

In the light of what we know today, as we shall see, there is nothing very surprising in this discovery. He was dealing not with a true solution of silver in water, but with a colloidal solution of the metal, and we today know colloidal solutions of the metals in great abundance. Bredig and others have prepared colloidal solutions not only of metals as insoluble as silver, but of far more insoluble metals such as platinum, iridium, gold, and the like.

This brings us down to the work which will be discussed in more detail in this book. The development of this new branch of solution has made necessary the introduction and use of certain terms, the meaning of which must be understood before the subject can be considered. As far as possible these will now be defined.

Nomenclature, Terms Introduced. — Several of the terms still in use were introduced by Graham in his classical researches on colloids. We have seen that he distinguished between *crystalloids* and *colloids*; the former diffusing readily through membranes of vegetable parchment, the latter diffusing only slowly or not at all through such membranes. The diffusion through the membrane he called *osmosis*. The separation of crystalloids from colloids by means of diffusion through such membranes, Graham termed *dialysis*; and the apparatus in which such separations were effected, a *dialyzer*.

He found that many substances which are ordinarily insoluble in water, such as arsenic trisulphide, silicic acid, etc., when prepared in certain ways, apparently dissolve in water. Thus, if hydrogen sulphide is added to a solution of arsenic chloride, the arsenic sulphide is precipitated as a yellow solid. If, on the other hand, an aqueous solution of hydrogen sulphide is added to an aqueous solution of arsenic oxide, no precipitate is formed; the arsenic sulphide thus produced remaining in solution, giving a yellowish color to the solution. Similarly, if hydrochloric acid is added to a strong solution of a soluble silicate, silicic acid is precipitated. If, however, hydrochloric acid in excess is added to a dilute solution of a soluble silicate, there is no precipitation of silicic acid, but the solution remains perfectly clear, indicating that the silicic acid formed remains in solution. Graham dialyzed such apparent solutions and found that the silicic acid was not present as a true solution, but was there as a *colloidal solution.*

When both of the constituents, solvent and substance, of a colloidal solution were liquid, Graham termed the system a *sol.* If one of the constituents was solid, the system appearing to be like a jelly, he termed this a *gel.*

Graham found that liquids other than water are capable of forming colloidal solutions. Thus, alcohol, glycerol, etc., could form such solutions. Colloidal solutions in water he termed *hydrosols* and *hydrogels*; in alcohol, *alcosols* and *alcogels*; in glycerol, *glycerosols* and *glycerogels.* So much for the nomenclature of colloidal chemistry as far as we owe it to Graham.

More Recent Terms. — As our knowledge of colloids has increased in recent times, it has been found necessary to supplement Graham's nomenclature with certain other terms. We shall see that the differences between true solutions, colloidal solutions, and colloidal suspensions, are vitally connected with the state of division of the dissolved substance. In a true solution the dissolved substance, if a non-electrolyte, is, as we have seen, usually in the molecular condition as shown by the determination of its molecular weight by the freezing-point or the boiling-point method. In colloidal solutions the particles are, as we shall see, much more coarse-grained. In colloidal suspensions they are still more coarse-grained, and in mechanical suspensions more coarse-grained than in colloidal suspensions. The degree of fine-grainedness or *dispersity* of the colloidal particles is then a matter of great importance in the chemistry of colloids.

If the dispersion is not great we have *emulsions* and *suspensions.* If the dispersion is great the dispersoids are divided into *emulsoids* and *suspensoids,* and these terms are frequently used in discussing colloids.

Nomenclature of Wolfgang Ostwald. — Wolfgang Ostwald would divide dispersoids as follows, depending on their degree of dispersity or fine-grainedness: (*a*) coarse dispersions (these include the emulsions and suspensions), (*b*) colloidal solutions proper (finer-grained), (*c*) molecular dispersoids (still finer-grained), (*d*) ion dispersoids (finest of them all). Group *b*, or colloidal solutions, includes emulsoids and suspensoids. The emulsoids, or emulsion colloids, in which the dissolved substance is liquid, show certain fairly characteristic properties. Among these are to be mentioned their high viscosity; under the ultramicroscope the individual particles can not, in general, be seen, there being only a general illumination of the field; very concentrated solutions of salts are required to coagulate them, and they are devoid of the interesting and important electrical properties, including the carrying of a charge, which are characteristic of the suspensoids.

The suspensoids or suspension colloids have also more or less well-defined and characteristic properties; their viscosity is not very different from that of the pure solvent; when examined under the ultramicroscope the individual light discs can be seen; they are readily coagulated by electrolytes and by whirling in a centrifuge; the parts are charged electrically, which we shall see is very important in determining the nature of colloidal solutions, as well as in the precipitation of the colloidal particles by electrolytes, and they show the Brownian movement. Good examples of the suspension colloids are the metal hydrasols, while gelatine solutions are examples of emulsoids.

While these groups of dispersoids are fairly distinct from one another, yet systems are known which correspond to transitions from the one to the other. A sol may have the properties of a gel, and *vice versa.* This apparent abnormality has been explained as due probably to attraction between the two phases present. Where such attraction exists the system has been called a *lyophile;* where it does not exist a *lyophobe.* We can have lyophiles and lyophobes in water, in alcohol, in glycerol, etc. In these cases they become *hydrophiles* and *hydrophobes, alcophiles* and *alcophobes, glycerophiles* and *glycerophobes,* etc.

As we have seen, we have both sols and gels, and each can pass into the other. When a sol passes into a gel, we speak of it as *gelation.* When a gel passes into a sol, we refer to it as *solation.*

With these terms clearly in mind we can now proceed to the study of the more recent work in the field of colloid chemistry, and shall take up first the methods which have been discovered and are used for preparing colloidal solutions in the broad sense of that term.

Methods of Preparing Colloidal Solutions. — A fairly large number of methods have been devised for preparing colloidal solutions. These admit of easy classification, in that they fall into two general classes — Chemical Methods and Electrical Methods.

The chemical methods include double decompositions — hydrolysis being a double decomposition in which water is one of the substances involved. Reductions are obviously chemical methods.

The electrical method, as we shall see, has come prominently into play in recent times.

Double Decompositions. — We have seen how Graham prepared colloidal silicic acid and colloidal arsenic sulphide.

These are simply examples of double decompositions which are so well known in chemistry. Other examples of methods involving simple double decomposition in which there is neither oxidation nor reduction, are the following. It is well known that whenever the salt of a weak acid or a weak base, or still better if the acid and base are both weak, is brought into the presence of water, the salt is in part hydrolyzed or broken down into the free acid and the free base. A fairly large number of bases have, in this way, been prepared in the colloidal condition.

Although hydrochloric acid is a strong acid, its salts with weak bases such as aluminium chloride and ferric chloride are more or less hydrolyzed by water, especially at more elevated temperatures, and the resulting hydroxides are in the colloidal condition.

Some nitrates are also hydrolyzed, and the resulting hydroxides are in the colloidal condition. If the acid is weak as well as the base the hydrolysis is greatly increased. Acetates are much more hydrolyzed than chlorides and nitrates, and the hydrolytic action of water on acetates has been used fairly extensively in the preparation of colloidal solutions of hydroxides. In this way colloidal solutions of iron and aluminium and other hydroxides have been prepared.

Reductions. — So much for the methods involving simple chemical double decompositions. Other chemical reactions have been used to prepare colloidal solutions. These involve reduction processes, and will be briefly considered. The reactions have to do primarily with the reduction of salts of the metals by certain reducing agents.

These reduction methods were the first to be used in preparing colloidal solutions. Thus, at the very beginning of the nineteenth century gold sols were prepared by reducing salts of gold with mild reducing agents.

Faraday,[1] in 1857, prepared gold sols by reducing auric chloride with yellow phosphorus dissolved in ether, and the soluble silver of M. Carey Lea,[1] already referred to, was prepared by reducing a silver salt with a concentrated solution of ferrous citrate.

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[1] *Phil. Trans.*, **147**, 145 (1857).

The history of the preparation of purple of Cassius is interesting. As is well known, it is formed when a dilute solution of a salt of gold is treated with stannous chloride.

The nature of this purple of Cassius has attracted the attention of chemists since the time of Berzelius, but only since colloidal chemistry came to the front has its real nature been understood. Gold sols have recently been prepared by reducing salts of gold with carbon monoxide. Zsigmondy has found formaldehyde a satisfactory reducing agent for preparing sols of gold from gold salts, while Gutbier has made use of the mild reducing agents hydroxylamine, phenylhydrazine, and hydrazine. He has also prepared by this method sols of the very resistant metals, platinum, iridium, etc. The Gutbier method gives colloidal solutions of the metals which are relatively stable, and when properly protected, persist for considerable periods of time.

Stable sols of platinum have also been prepared by reducing its salts with acroleïn.

A few colloidal solutions have been made by the opposite of reduction methods, viz., oxidation methods; but these are not sufficiently important to call for any detailed discussion here.

Electrical Methods. — It was known to Humphrey Davy that when a heavy electrical discharge is passed between metal poles, the metal particles are torn off in a fine state of division.

Utilizing this fact, Bredig[2] has devised a method for preparing colloidal solutions of many of the most resistant metals. If it is desired to prepare a platinum sol, two stout wires of platinum are dipped into pure water, and the terminals brought sufficiently close together so that an electric arc is set up between them when the proper electromotive force is impressed upon the metal wires. Under these conditions the metal in question is torn off in a very fine state of division, and remains suspended in the water as a sol of the metal in question. In this way Bredig, using a current from 30 to 110 volts, and from 5 to 10 ampères, was able to prepare sols of platinum, iridium, silver, and gold.

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[1] *Amer. Journ. Science*, **37**, 476; **38**, 47 (1889).

[2] *Zeit. phys. Chem.*, **31**, 258 (1899).

The method of Bredig worked very well in water, but when other liquids, especially the organic, were employed, it did not give such satisfactory results. The liquids themselves often underwent decomposition, liberating carbon which was admixed with the sol in question.

The Bredig method, as modified by Svedberg,[1] overcame some of these difficulties, and enabled sols to be prepared in solvents other than water.

The surface of the metal of which it was desired to prepare a sol was increased. A condenser was introduced into the circuit and a very small current of 50 or less milliampères was employed. Later Svedberg used an inductorium which gave an alternating current. With this improved method he prepared sols of silver, tin, gold, etc., in several solvents.

He prepared sols of all of the alkali metals in ethyl ether as well as a large number of metal sols in isobutyl alcohol. He obtained sols not only of most of the metals, but of selenium, carbon, silicon, etc., and of a number of minerals.

PROPERTIES OF COLLOIDAL SOLUTIONS

The three most characteristic properties of true solutions are: osmotic pressure, lowering of freezing-point, and rise in boiling-point. These properties are not only possessed by all true solutions, but they obey certain well-defined laws. Thus, the osmotic pressures of true solutions obey the laws of gases, as we have already seen. The lowering of the freezing-point of the solvent, and the rise in its boiling-point produced by dissolved substances, are in accord with the well-known laws of Raoult dealing with these phenomena. Given a system which appears to be a true solution, the question is, how can we determine whether or not it is a true solution? Knowing its concentration, we measure its osmotic pressure, its freezing and boiling-point, and see whether all of these conform to the well-known laws of true solutions.

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[1] *Ber. d. chem. Gesell.*, **38**, 3616 (1905); **39**, 1705 (1906). *Koll. Zeit.*, **1**, 229, 257 (1907).

One of the first questions that would naturally arise in connection with colloidal solutions is, do they have these three properties at all, and if so, to what extent?

Osmotic Pressures of Emulsions and of Suspensions.—The above question resolves itself into two. Do emulsoids or emulsion colloids have osmotic pressure, and if so to what extent? Do suspensoids show osmotic pressure, and if so what is its order of magnitude? Take first the emulsions. Pfeffer measured the *osmotic pressures of a few colloids* and found values which are very small as compared with crystalloids.

Rodewald and Kattein[1] measured the osmotic pressures of the starch iodine emulsoid. A sol containing about 30 grams to the liter gave an osmotic pressure of approximately 20 cm. of water.

The most elaborate work in this field is perhaps that of Lillie,[2] who studied the osmotic pressures of a number of emulsoids. He found that a solution of egg albumin containing 12.5 grams to the liter showed, at ordinary temperatures, an osmotic pressure of about 20 mm. of mercury. When the osmometer reached this height it stood constant for a considerable period of time. This fact is of importance as bearing on the question as to whether the osmotic pressure actually observed was due to the emulsoid itself, or to some crystalloid impurity mixed with it. If it were due to some crystalloid mixed with the colloid, then on standing in contact with the membrane this would have diffused out of the colloid through the membrane, and the pressure registered on the osmometer would not have remained constant over any considerable period of time. The fact that this pressure did remain constant indicates that it was due to the emulsoid itself. The only alternative seems to be to assume that it is due to some admixed crystalloid which is so held by the colloid that it cannot diffuse out of it through the membrane. This alternative seems to be scarcely acceptable. When we take into account the further fact that an emulsoid prepared in a number of different ways, and therefore, which could not contain even the same crystalloid, much less the same or comparable amounts of crystalloids, shows the same osmotic pressure, we are almost forced to the conclusion that the osmotic pressure in question is due to the emulsoid, and not to some admixed impurity.

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[1] *Zeit. phys. Chem.*, **33**, 588 (1900). [2] *Amer. Journ. Physiol.*, **20**, 127 (1907).

When we turn to suspensoids the results of the direct measurements of osmotic pressure are less satisfactory. Linder and Picton[1] worked with sols of ferric hydroxide and arsenic trisulphide, attempting to measure directly their osmotic pressures. They were not able to obtain concordant results. If these systems have osmotic pressures it can be said that these pressures are very small. This may be due in part to the relatively large sizes of the particles in a colloidal suspension.

Lowering of Freezing-Point and of Vapor Tension. — The freezing-point lowerings and lowerings of vapor-tension or rise in boiling-point, produced even by emulsoids, must of necessity be small, since the osmotic pressures are so small. This will be obvious when we consider that an osmotic pressure of 1 mm. of mercury corresponds to only about one ten-thousandth of a degree lowering of the freezing-point. Bruni and Pappada[2] prepared some very pure sols of albumin, gelatine, etc., and were unable to detect any difference between their freezing-points and boiling-points, and those of pure water. This shows how meaningless are a number of the attempts that were made to determine the molecular weights of colloids by the freezing-point and the boiling-point methods. Enormous molecular weights were found for many colloids, and their molecular weights may be relatively enormous, but there is no necessary connection between the molecular weights found by these methods and the true molecular weights of these substances. It is highly probable that in most cases the lowering of the freezing-point and the rise in the boiling-point observed, were due to crystalloid impurities in the colloids. Further, if the colloids themselves actually produced the phenomena observed, it is not at all certain that these properties could be used to determine the molecular weights of these colloids. Before this can be done it must be shown that Raoult's laws of freezing-point lowering and depression of vapor-tension, or rise in boiling-point, hold for colloids as well as for crystalloids.

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[1] *Journ. Chem. Soc.*, **87**, 1906 (1905).

[2] *Rend. R. Acc. dei Lincei* [5], **9**, 354 (1900).

If these methods cannot be used to determine the molecular weights of emulsoids, still less can they be employed with suspensoids, which show still smaller depression of the freezing-point and rise in the boiling-point, if they have these properties at all.

Diffusion of Colloids. — If we recall the relations already pointed out when we were considering true solutions, between diffusion and osmotic pressure, viz., that all diffusion is caused by osmotic pressure, we should expect to find all colloids diffusing very slowly, if diffusing at all. Such was shown to be the case by Graham in his classical researches on colloids. Indeed, his fundamental method of distinguishing between crystalloids and colloids was based upon the powers of these two classes of substances to diffuse, or not to diffuse, through vegetable parchment.

We have seen that the emulsoids show greater osmotic pressures than the suspensoids and we should expect them to diffuse more rapidly. Such is the fact. Herzog[1] has determined the relative rates of diffusion of a number of colloids as compared with certain organic crystalloids and a few of his results are given below.

	Diffusion constant
Urea	1.01
Glucose	0.57
Pepsin	0.063
Albumin	0.054
Emulsin	0.036

These suffice to show the relative slowness with which the colloids diffuse, and these colloids are emulsoids. Since suspensoids have smaller osmotic pressures than emulsoids we should expect them to diffuse even more slowly, and here again the facts are in accord with prediction. Indeed, some experiments have been carried out which would seem to make it doubtful whether certain suspensoids, at least under certain conditions, diffuse at all.

Brownian Movement. — The English botanist R. Brown[2] as early as 1827 observed that the pollen grains of plants, when suspended in water, were continually in a state of oscillatory motion. He observed that this was a general phenomenon. Very finely divided solid particles suspended in any liquid which was not too viscous, showed these movements. From the name of the discoverer this has come to be known as the Brownian movement.

It was at first thought that these movements might be due to some cause external to the liquid, such as jarring, changes in temperature producing currents in the liquid, etc. This was tested by working in places free from mechanical disturbance and at a constant temperature. The movements of the particles under these conditions were essentially the same as when less precautions were taken, as was shown by Wiener.[1] The persistence of the Brownian movement unchanged for apparently unlimited periods of time, shows that it could not be due to external conditions which are constantly changing.

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[1] *Zeit. Elektrochem.*, **13**, 533 (1907).

[2] *Pogg. Ann.* **14**, 294 (1828).

Distance Traveled and Velocities of the Particles. — The *distance* through which the particles move depends largely upon their size. Particles having a diameter of about 1 μ, oscillate along a path which has a length of about 2 μ; smaller particles, as we shall see, move through much longer paths. This will be discussed under the results of work with the ultramicroscope.

The velocities with which the particles move are also a function of their size. Exner[2] showed that particles ranging in diameter from 0.4 to 1.3 μ move with a velocity of from 3.8 to 2.7 μ per second. Very much smaller particles as seen under the ultramicroscope move with velocities as much as thirty times greater. This also will be discussed when the results of ultramicroscopic investigations are considered.

Not only the size of the suspended parts determines the lengths of the paths they travel and the velocities with which they move, but, as we would expect, the *nature of the medium* in which the parts are suspended exerts a pronounced influence.

Svedberg[3] has established two generalizations connecting the nature of the medium with the motions of the particles suspended in it. The first connects the amplitude of the vibrations with the viscosities of the media. The generalization in question is[4] for particles of a given size, "if the amplitudes (of vibrations of the particles) are plotted as ordinates, and the viscosities of the media as abscissae, the curve takes the form of a hyperbola." This means that the amplitude is inversely proportional to the viscosity.

The other relation has to do with the time required for a particle to move along its path and the velocity with which it travels. "The velocity[1] in solvents of very different nature is nearly constant and has the value 2 to 4×10^{-2} centimeters per second."

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[1] *Pogg. Ann.*, **118**, 79 (1863).

[2] *Ann. d. Phys.* **2**, 843 (1900).

[3] *Zeit. Elektrochem.*, **12**, 853, 909 (1)906.

[4] *Ibid.*, 854 (1906).

The time of oscillation is approximately proportional to the amplitude. Temperature has a marked effect. Exner[2] has shown that between the temperatures 20° and 70°, the square of the velocities is proportional to the temperature.

Cause of the Brownian Movement. — So much for some of the facts pertaining to the Brownian movement. The important question still remains, what causes these movements? We have seen that they cannot be due to such external causes as jarring, changes in temperature, etc. Since these movements are not due to external causes, their cause must be sought for within the liquid itself. In the opinion of Ramsay,[3] Einstein[4] and others, the Brownian movement is due to the impacts or blows of the molecules of the liquid against the solid suspended particles. From the mathematics of chance, we might naturally think that as many liquid molecules would strike the particle in any given unit of time on the one side as on the other, and the result would be that the particle would remain at rest. Such would probably be the case if we think of a long period; but for a relatively short period a particle would be hit on one side by a larger number of molecules than on the other, and, consequently, motion would result.

Work of Perrin. — The theory of the Brownian movement has been worked out by Einstein and Smoluchowski. It has been studied experimentally by Ehrenhoft, Svedberg, and by Perrin. The work of the last named has attracted so much attention that one phase of it will be considered in some detail. Perrin undertook his work to determine the cause of the Brownian movement, and to find out whether an emulsion obeyed the gas laws as true solutions do. He reasoned that if large molecules such as cane sugar, quinine sulphate and the like, in true solutions, obeyed the gas laws as well as molecules of smaller molecular weights, then there seemed to be no *a priori* reason why the grains of an emulsion should not obey these same laws.

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[1] *Zeit. Elektrochem.*, **12**, 859.

[2] *Ann. d. Phys.*, **2**, 843 (1900).

[3] *Chem. News*, **65**, 90 (1892).

[4] *Ann. d. Phys.*, **19**, 371 (1906).

If an emulsion obeys the gas laws, and we allow a uniform emulsion to come to equilibrium at constant temperature, the grains ought to distribute themselves in the emulsion according to the height, just as in the case of a column of gas or in the atmosphere.

On the assumption that the gas laws hold for emulsions, Perrin deduced the following equations,[1]

$$2.30\ W \log \frac{n_o}{n} = 2\pi a^3(\Delta - d)\ gh$$

in which W is the mean granular energy, n and n_o the concentrations at the two different heights, a the radius of the grains, Δ the density of the grains, d the density of the liquid, g the pull of gravity and h the difference between the two heights.

From the gas laws $W = \frac{3RT}{2N}$. Substituting,[2] we have

$$2.30\ \frac{RT}{N} \log \frac{n_o}{n} = \tfrac{4}{3}\ \pi a^3\ (\Delta - d)\ hg$$

which enables us to calculate the Avogadro constant N.

Perrin prepared emulsions in water of gamboge and of mastic, and by fractional centrifuging he was able to obtain them practically uniform. He determined the density of the grains by two methods. First, he dried the grains to constant weight at about 110°, and then heated them higher, when a viscous liquid resulted, which, on cooling, formed a transparent glass. The density of this was obtained by suspending in a solution of potassium bromide of known concentration. Secondly, at a given temperature he obtained the mass m of water, and m' of emulsion filling an equal volume. By drying, he found the mass n of the resin contained in m' of emulsion; the mass of the intergranular water being $m' - n$. If d is the absolute density of water, the volume of water having a mass $m = \frac{m}{d}$; and that of intergranular water $= \frac{m' - n}{d}$. The difference, $\frac{m}{d} - \frac{m' - n}{d}$, is the volume of the grains, and n divided by this volume, their density. The values obtained by these two methods are concordant.

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[1] *Ann. Chim. Phys.* [8], **18,** 32–36 (1909).

[2] *Ibid.,* p. 62.

Concentrations of the Colloids at Different Levels. — To obtain n and n_o, Perrin used a small cell $\frac{1}{10}$ mm. deep, into which was introduced a drop of the emulsion. This was covered with glass to prevent evaporation. It was placed under a microscope; the objective, while having great magnifying power, had only a small depth of field, so that only the granules in a layer $\frac{1}{100}$ mm. in thickness could be clearly seen. By raising and lowering the microscope, grains at different levels could be observed and the height read on a micrometer screw. Of the larger grains Perrin was able to obtain photographs at the different levels, but with the smaller he was compelled so to reduce the field that only a few grains could be seen at any one time. The ratio between the mean numbers of grains seen at the two heights would, of course, give the ratio of the two concentrations, $\frac{n_o}{n}$.

Radii of the Particles. — Perrin obtained the radii of the particles, a, by three different methods.

First, he applied the law of Stokes for bodies falling in a liquid.

$$6\pi\eta a v = \tfrac{4}{3}\pi a^3(\Delta - d)g$$

in which η is the viscosity of the medium, v, the velocity of fall, and Δ and d the densities of grains and medium respectively. The rate at which the particles fell or settled he determined as follows. He placed some of the emulsion in a capillary tube, kept the temperature constant, and noted the rate at which the emulsion cleared. The other factors are known and a could be calculated.

Secondly, Perrin counted the number of grains in a known volume of emulsion, which gives the mass of a grain, and, the density being already known, also the radius. The counting was made possible by the fact that if the emulsion is rendered slightly acid, the grains, when they come close to the wall, adhere to it, and being at rest, can be counted.

The third method is based upon the fact that when a drop of the emulsion is allowed to evaporate on a micrometer objective, the grains arrange themselves in lines which can be measured; and by dividing by the number in the line we obtain the diameter and therefore a.

These three methods gave concordant results, showing that the law of Stokes can be applied to emulsions.

Perrin found that it was a comparatively simple matter to verify the law that at equal elevations there were equal rarefactions. He used grains whose radii varied as much as one to forty. He used different resins, varying the viscosity, but always obtained concordant results. He found for the value of n, 70.5×10^{22}, and for the weight of the hydrogen atom in one case 1.47×10^{-24} grams, which agrees closely with the value 1.6×10^{-24}, which was derived from the equation of Clausius and Maxwell. This is good evidence that the Brownian movement is to be explained by the kinetic theory.

Mass of the Atom. — Perrin studied the Brownian movement to determine the mass of the atom. Using the equation of Einstein, which involves the mean displacement of the grain in a given time and the mean energy of rotation, he obtained for the weight of the hydrogen atom the values 1.45×10^{-24}, and 1.56×10^{-24}. Perrin summarizes his work and results as follows:

(1) The preparation of uniform emulsions, chosen at will and measured exactly.

(2) Extension of the law of Stokes to microscopic dimensions.

(3) Demonstration that the gas laws apply to uniform emulsions.

(4) Determination of the weights of atoms and molecules.

(5) Experimental confirmation of the theories of Einstein.

THE ULTRAMICROSCOPE

We have learned that by means of the microscope we can see the small particles in many emulsions and observe their Brownian movement. In many emulsions the particles are too small to be seen, even with the most powerful microscope. A very important advance has been made in this field by the discovery of the ultramicroscope. We owe this discovery primarily to Zsigmondy and Siedentopf.[1] Another form of ultramicroscope was developed in the same year by Cotton and Mouton.[2]

Principle of the Ultramicroscope. — When a beam of light is passed through dust-free air, and an attempt made to observe it in a direction at right angles to the beam, nothing is seen. If the air contains particles of dust, these reflect the light and the beam is readily seen.

Similarly, when a beam of light is passed through a perfectly clear solution, and an attempt made to observe the beam in a direction at right angles to that of propagation, nothing is seen. If, on the other hand, the liquid contains suspended particles, these disperse the light, and the path of the beam through the liquid can readily be seen. This is what is known as the Tyndall effect. It would seem only natural to apply the principle illustrated by this effect to the study of colloidal solutions; especially to those in which the particles are too small to be seen by the microscope; the limit of microscopic visibility being about 0.15 μ.

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[1] *Ann. d. Phys.*, **10**, 1 (1903).

[2] *Compt. Rend.*, **136**, 1657 (1903).

It was shown by Fizeau[1] and by Ambronn[2] that beams of light so narrow that they fell below the limit of the microscope, could be seen. This suggested to Zsigmondy that the particles in a colloidal solution which were too small to be seen by the microscope, might reflect enough light to be visible.

The Zsigmondy Apparatus.[3] — The apparatus at first designed by Zsigmondy may be roughly described as follows. A beam of sunlight is reflected by a mirror through a lens, which focuses it just under the objective of a microscope, in a colloidal solution contained in a cell with glass walls.

With this apparatus Zsigmondy, in 1900, studied colloidal solutions of gelatine, glue, etc., and observed the spots of light reflected from the individual particles of the colloid. In emulsions in which the particles were very small, the light reflected from the individual particles could not be seen.

Having found that particles which are submicroscopic can be rendered visible by side illumination in an otherwise dark field, Siedentopf and Zsigmondy took up the question of perfecting the apparatus, to render visible still smaller colloidal particles.

The improved form of the ultramicroscope of the above named investigators is based primarily upon two fundamental principles.

(*a*) The particles must be illuminated as intensely as possible, care being taken that none of the light falls directly upon the eye. Only the light *reflected* from the colloidal particles passes up through the microscope into the eye.

(*b*) The field of the microscope must be kept dark, the only light entering it being from the side, as already discussed.

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[1] *Pogg. Ann.*, **116,** 473 (1862).

[2] *Wied. Ann.*, **48, 717** (1893).

[3] For details see *Colloids and the Ultramicroscope*, by Zsigmondy; translated by Alexander (Longmans).

The Siedentopf Ultramicroscope. — The apparatus designed by Siedentopf[1] contains the following essential parts. A beam of sunlight allowed to enter a darkened room passes through a telescope objective of focal length about 10 mm., and casts an image of the sun having a diameter of about 1 mm. on a slit which admits of careful adjustment. The width of the slit can be easily measured. In the path of the light there is a second telescope objective having a focal length of about 80 mm. The light thus passes through a microscope objective which projects it into the colloidal solution contained in the glass cell. It is reflected from the colloidal particles upward through a microscope into the eye.

Nomenclature of Ultramicroscopy. — The study by means of the ultramicroscope of particles too small to be seen by the ordinary microscope, has made it desirable, indeed necessary, to extend the nomenclature of microscopy.

Siedentopf terms a particle which is too small for ordinary microscopic resolvability, *ultramicroscopic.* This term applies to particles whose diameter is less than one-fourth μ.

If the ultramicroscopic particle can be rendered visible it is termed *submicroscopic,* and such a particle is a *submicron.*

If the ultramicroscopic particle cannot be rendered visible it is termed *amicroscopic,* and such a particle an *amicron.*

Results Obtained with the Ultramicroscope — Sizes of the Colloidal Particles. — One of the first problems in using the ultramicroscope is to obtain the liquid as nearly as possible transparent. Ordinary distilled water does not fulfill this condition. It contains colloidal particles or dust particles which interfere with its use in ultramicroscopy. In studying particles which are so small that they are barely visible, it is very desirable to obtain water which shows no light-cone. This is accomplished by redistilling the water, and allowing it to stand for some time in a space free from dust.

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[1] *Druckshe. Verz. opt. Werk., C. Zeiss,* 164 (1904).

One of the most interesting applications of the ultramicroscope is to the problem of the *size of colloidal particles.* Siedentopf and Zsigmondy[1] have described two methods for determining their sizes.

If we represent the mass of the colloidal substance in solution by m, the number of colloidal particles by n, and the density of the colloidal substance by d, the volume of a single particle, v, is calculated from the following equation —

$$v = \frac{m}{dn}$$

m, the mass of the substance in a given volume of the solution is obtained directly, knowing the concentration. The number of particles, n, in this volume is counted by means of the ultramicroscope, the density, d, of the substance from which the colloid is made being determined in the usual way. All of the quantities in the above equation are known except v, which is, of course, calculated at once. The dispersity of a sol is usually expressed in terms of the diameter, which is calculated from the volume on the assumption that the particle is a cube or a sphere.

In counting the number of particles in a given volume, the colloidal solution must be so dilute that the number in the illuminated field is very small. If this is not so, the continuous and comparatively rapid motion of the particles obviously would make it impossible to count them. When favorable conditions have been secured, the accuracy of this method is placed by Siedentopf at about twenty percent.

The second method of determining the size of the particles is based upon the expression —

$$v = \frac{mr^3}{d}$$

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[1] *Colloids and the Ultramicroscope,* p. 117.

All of the symbols have the same significance as in the former expression; the new symbol r being the average distance between the particles. The layer studied must be accurately measured and the mean of a number of results is usually taken. The depth must be as great or greater than the distance between the particles. The smallness of the particles which can be seen depends largely upon the illumination; and, as we would expect, somewhat upon the nature of the particles. When the source of the illumination is an electric light the smallest gold particles that can be seen have a diameter of 15 $\mu\mu$, which is 15×10^{-6} mm. When very bright sunlight is used particles can be seen which are as small as 5 $\mu\mu$.

As Zsigmondy points out, the difference between the index of refraction of gold and that of water is very great, which, of course, aids ultramicroscopic visibility. Particles of very few substances less than 15 $\mu\mu$ in diameter can be seen with the ultramicroscope with an electric light, and perhaps none smaller than 5 $\mu\mu$ with the aid of sunlight. This shows how entirely erroneous is the view that with the ultramicroscope molecules or ions of any substance can be seen.

Motion of Emulsion Particles. — We have seen what is meant by the Brownian movement of suspended particles. The question arises, are the particles in an emulsion in motion? If so, how do they move? Zsigmondy has described what he observed. The particles move very rapidly in very irregular paths; indeed, so rapidly that the Brownian movement of the larger suspended particles is slow by comparison. The small particles in a gold hydrosol show both translatory and oscillatory motion. The translatory motion is from one hundred to one thousand times the diameter of the particle. This takes place in about one-seventh of a second. The oscillatory motion has a much shorter time period.

The velocities with which the smaller gold particles move are thus incomparably greater than the Brownian movements of larger suspended particles. The motion of the smaller particle of gold seems to differ from the Brownian movement of larger suspended particles in the character of the paths which they describe, as well as in the velocities with which they move.

We have seen that the Brownian movement becomes slower and slower the larger the suspended particles. Just so it is with the motions of the particles of gold in a gold hydrosol. The motion becomes slower and slower the larger the size of the particles. Zsigmondy at one time seemed to think that the motion of the small gold particles in a gold sol was something quite different from the ordinary Brownian movement. He studied the cause of these movements.

Under the ultramicroscope the gold sol is illuminated from the side. This might produce unequal heating in the sol and thus give rise to motion. Zsigmondy passed the light through water before allowing it to enter the sol. He thus cut out the heat rays, but observed the same motions of the gold particles.

He went further. He illuminated the field for different periods of time, but this produced no effect on the motions; showing that the cause of the motion must be sought for within rather than without the colloidal solution.

Zsigmondy seems to think that the fact that the gold particles are charged with one sign and the water about them with the other, has much to do with the motions of these particles. This fact must certainly be taken into account in dealing with this phenomenon.

On the other hand, it may be shown that the movements of the fine particles in an emulsion are little or nothing else than very rapid Brownian movements.

ELECTRICAL PROPERTIES OF COLLOIDS

When we were studying true solutions we saw that their electrical properties were among the most interesting and important. The question of carrying or not carrying an electrical charge was the distinguishing feature between electrolytes and non-electrolytes in solution. By this property primarily, all chemical compounds were divided into these two great classes. The cause of the marked differences between the two was found in the fact that the electrolytes in the presence of water and other dissociating solvents, break down into charged parts or ions; the cations carrying positive charges and the anions negative charges. The non-electrolytes are not thus dissociated, remaining in solution in the molecular condition.

We have seen how fundamentally different the properties of these two great classes of substances are, and how these differences are to be referred to the charged ions on the one hand, and to the uncharged molecules on the other.

The question of the colloidal particles being charged or uncharged, is quite as fundamental for colloids as for true solutions of electrolytes and non-electrolytes. The charges on the colloidal particles not only determine many of their physical properties but, as we shall see, the stability of the colloid itself.

Electrical Endosmosis. — This term is applied to the passage of a liquid through a diaphragm, or through capillary tubes, when a current is passed between two electrodes placed the one at each end of the tube. Take a U-shaped glass tube[1] and place at the bottom of the U a bundle of short capillary tubes. Insert one electrode at each end of the tubes and pass a current from one to the other through the liquid which fills the U-tube. The liquid will rise in one of the arms of the U-tube, which one depending on the direction in which the current is passed, until it stands at a higher level in one arm than in the other. For a definite difference in potential between the electrodes the liquid will rise to a definite height in the one arm, establishing a definite difference in level in the two arms, when equilibrium will be reached. This phenomenon seems to have been observed for the first time by Reuss.[1] It was subsequently studied by G. Wiedemann[2] and by Quincke,[3] and later investigated quantitatively and mathematically by Helmholtz.[4] Perrin[5] has quite recently worked out the theory of the process.

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[1] Freundlich: *Kapillarchemie*, p. 224 (1909).

The height to which the liquid will rise, or the difference in level of the liquid in the two arms of the U-tube already referred to, is, as would be expected, proportional to the electromotive force impressed upon the electrodes.

A large majority of substances when brought in contact with water become charged negatively — the water positively. Under these conditions water would of course go to the cathode. If the substance in question, when brought in contact with water, should be charged positively, the water would be charged negatively and go to the anode.

The effect of electrolytes — acids, bases and salts — on electrical endosmosis has been studied by Perrin and others. He found that acids render negative diaphragms less negative and positive diaphragms more positive. Alkalies, on the contrary, render negative diaphragms more negative, and positive diaphragms less positive. Very small concentrations of electrolytes produce a marked effect on electrical endosmosis. A relation of interest and of some importance has been worked out between the valency of the ions and the action of salts yielding these ions on the difference in potential which exists between the liquid that is present and the solid. When the diaphragm is negative, the valence of the cation present conditions the difference in potential. When the diaphragm is positive, the valence of the anion determines the potential difference.

These relations are valuable in connection with the precipitation of colloids by electrolytes.

Cataphoresis. — We have seen that the movements of liquids through diaphragms and capillary tubes under an impressed electromotive force is known as electrical endosmosis. The movements of the solid suspended particles through the liquids in which they are suspended, under the action of an external electromotive force, is known as cataphoresis. The migration of the suspended parts to the poles is, in a sense, analogous to the migration of the ions in a true solution when an electromotive force is impressed upon the solution.

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[1] Wiedemann: *Elektrizität,* I, 993 (1893).

[2] *Pogg. Ann.*, **87**, 321 (1852).

[3] *Ibid.*, **113**, 513 (1861).

[4] *Ges. Abhl.* I, 855.

[5] *Journ. Chim. Phys.*, **2**, 601 (1904).

This phenomenon seems to have been observed first in the cases of arsenic sulphide and ferric hydroxide sols by Linder and Picton.[1]

The *negative sols* or those which migrate to the positive pole, or anode, include the metals silver, gold, platinum, etc., and most of their compounds except their oxides and hydroxides; the trisulphides of arsenic and antimony; the non-metals sulphur, selenium and tellurium and such colloids as gamboge, mastic, eosin, aniline blue, indigo, etc.

The *positive sols* or those which move to the negative pole or cathode, include the hydroxides of aluminium, iron, chromium, cadmium, zinc, zirconium, etc.; colloidal solutions of methyl violet, methylene blue, etc., and such metals as iron, lead and bismuth.

The determination of the *velocities* with which the particles move in cataphoresis is not a difficult matter. The method is analogous to that employed in determining the absolute velocities with which ions move. Electrodes are inserted into the two ends of a vertical tube containing the sol, and the current passed in the direction so that the colloid will move to the electrode in the lower end of the tube. In settling, the colloid possesses a sharp upper surface, which can be seen readily and with sufficient accuracy. The distance which it settles in a given time, under a given fall in the potential, can easily be measured.

Cotton and Mouton[2] have measured the velocity with which a single particle moves by observing it under a microscope provided with a micrometer eyepiece. In this way the distance traveled in a given time under a given potential gradient could be readily ascertained.

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[1] *Journ. Chem. Soc.*, **61**, 148 (1892).

[2] *Journ. Chim. Phys.*, **4**, 365 (1906).

In case the particle is submicroscopic, the ultramicroscope could and has been used.

Velocities with Which the Particles Move. — A few of the results[1] obtained in the study of cataphoresis are given below.

Suspended substance	Diameter of the parts	Velocity cm./sec. for unit potential gradient
Lycopodium	35 μ	25×10^{-5}
Arsenic trisulphide	50 $\mu\mu$ (about)	22×10^{-5}
Quartz	1 μ	30×10^{-5}
Berlin blue (colloid)	< 100 $\mu\mu$	40×10^{-5}
Gold (colloid)	< 100 $\mu\mu$	40×10^{-5}
Platinum (colloid)	< 100 $\mu\mu$	30×10^{-5}
Silver (colloid)	< 100 $\mu\mu$	23.6×10^{-5}
Bismuth (colloid)	< 100 $\mu\mu$	11.0×10^{-5}
Lead (colloid)	< 100 $\mu\mu$	12.0×10^{-5}
Iron (colloid)	< 100 $\mu\mu$	19.0×10^{-5}
Ferric hydroxide (colloid)	< 100 $\mu\mu$	30.0×10^{-5}

It is of interest to note that the velocities of the particles are nearly constant, independent of their nature and size.

We have seen what is the effect of the addition of electrolytes to electrical endosmosis. The same question arises here; but since electrolytes precipitate so many colloidal solutions, it is very difficult, not to say impossible, to answer it in any broad way.

Cataphoresis with Emulsoids. — The particles of emulsoids under the action of an electromotive force also move, but the motions are less definite and the phenomena more complicated than with suspensoids. The emulsoids are more likely to be precipitated, and the particles move more slowly than with suspensoids. The migration velocity of the particles of gelatine is only 25×10^{-5}.

The same emulsoid particle under one set of conditions may move in one direction, under other conditions, in the opposite direction, showing that it may be charged either positively or negatively. Thus, if the solutions are neutral, egg-albumin does not move in either direction, showing that it is electrically neutral. Perrin[1] has shown that in alkaline solution it goes to the anode, having a negative charge; in acid solution to the cathode, having a positive charge. The attempt to explain these phenomena as due to the amphoteric character of albumin meets with objections.

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[1] Freundlich: *Kapillarchemie*, p. 234 (1909).

Electrical Properties of Colloids in Non-aqueous Solvents. — The electrical phenomena in non-aqueous solvents are in many cases more complex than in water. Perrin[2] found that there is no electrical endosmosis in such solvents as carbon disulphide, chloroform, ether, benzene, oil of turpentine, etc. He observed pronounced endosmosis in such solvents as water, methyl alcohol, ethyl alcohol, acetone, nitrobenzene, etc. It will be recognized at once that the latter class of solvents have high *dielectric constants,* and therefore great dissociating power, hence this relation is of interest and importance. Those solvents with high dielectric constants show pronounced electrical properties.

Baudouin[3] showed that substances which in water are positive, are also positive in methyl alcohol — a liquid which also has a high dielectric constant; and the converse is also true.

Quincke[4] proved that cataphoretic phenomena in non-aqueous solvents in general run parallel with electrical endosmosis. Burton[5] demonstrated that the effect of temperature on electrical phenomena in non-aqueous solvents is largely the effect of temperature on the viscosity of the liquid. The explanation of the phenomena of electrical endosmosis and cataphoresis belongs to the future. We are not yet sufficiently familiar with the facts to reach any satisfactory generalization which would correlate them.

[1] *Compt. Rend.*, **136,** 1388 (1903).

[2] *Journ. Chim. Phys.*, **2,** 601 (1904).

[3] *Compt. Rend.*, **138,** 898 (1904).

[4] *Pogg. Ann.*, **113,** 513 (1861).

[5] *Phil. Mag.* [6], **11,** 441 (1906).

Electrostenolysis.—This term is applied to those phenomena which manifest themselves when an electric current is passed through fine cracks filled with a solution of an electrolyte. These phenomena have been studied by Brown.[1] Under these conditions metal often separates in the cracks, and the metal usually contains a large amount of hydrogen gas. Brown points out that under the conditions of such experiments — strong current and high resistance — the solutions of the electrolytes in the cracks are highly heated. The liquids in question decompose, liberating hydrogen gas which reduces the salts of the metals.

Conductivity of Suspensions. — The conductivity of suspensions is always greater than that of the water in which the parts are suspended. Whitney and Blake[2] purified certain sols until their conductivity did not further change with dialysis. They obtained the following results.

	Conductivity of the sol.	Conductivity of the water.
Gold sol.	12.7×10^{-6}	1.5×10^{-6}
Platinum sol.	2.9×10^{-6}	1.1×10^{-6}
Ferric hydroxide sol.	35.7×10^{-6}	

While the conductivities of the colloidal particles are small, they are much larger than that of the water in which they are suspended. This raises the question whether the conductivity may not be due to electrolytes held so firmly by the colloids that they cannot be separated by dialysis; and this question might be difficult to answer were it not for the following fact. When the current is passed the colloid particles move to the electrodes. In moving to the electrodes they must carry electricity and therefore take part in conduction.

This same question was tested by Duclaux[3] in the following manner. He filtered out the suspended particles and determined the conductivity of the filtrate. It was found to be less than that of the original sol, showing that the colloidal particles had some conducting power.

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[1] *Wied. Ann.*, **42**, 450 (1891); **44**, 473 (1891).

[2] *Journ. Amer. Chem. Soc.*, **26**, 1339 (1904).

[3] *Journ. Chim. Phys.*, **5**, 29 (1907).

The same point was tested by Whitney and Blake. They determined the conductivity of a gold sol. They then separated a part of the gold by cataphoresis, and redetermined the conductivity of the sol, and found that it had decreased. This was repeated five times, with the result that as more and more of the gold was precipitated from the sol, the conductivity became less and less. This is shown by the following results.[1]

	Conductivity
Gold sol. dialyzed	13.2×10^{-6}
After one cataphoresis	7.7×10^{-6}
After two cataphoreses	4.2×10^{-6}
After three cataphoreses	2.7×10^{-6}
After four cataphoreses	2.1×10^{-6}
After five cataphoreses	1.8×10^{-6}

Taking all of these results together, it seems fairly certain that suspensions have some conductivity.

Electrical Properties of Emulsions. — While the conductivity of pure emulsoid sols is always small, yet it is often appreciable. Whitney and Blake[2] measured the conductivity of the sol of silicic acid and found the value of 100×10^{-6}. For a gelatine sol they obtained the value 68×10^{-6}. The cataphoretic phenomena presented by these substances are in keeping with their conductivities.

Pauli,[3] on the other hand, freed albumin very carefully from electrolytes and studied its conductivity. It was found to be practically a non-conductor. It showed practically no cataphoresis. When a tension of 250 volts was impressed upon it, the particles did not migrate.

Emulsoids with respect to conductivity fall, then, into two classes; those that show quite appreciable conductivity, and those that show little or none.

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[1] *Journ. Amer. Chem. Soc.*, **26**, 1346 (1904).

[2] *Ibid.*, 1374 (1904).

[3] *Beitr. chem. Physiol. u. Pathol.*, **7**, 531 (1906).

PRECIPITATION OF COLLOIDS BY ELECTROLYTES

This brings us to one of the most interesting and important chapters of colloid chemistry; interesting because it throws light on the whole subject of precipitation in chemistry, and important as telling us something about the nature of colloids themselves. We shall consider first the action of electrolytes on suspensoids, and then their action on emulsoids.

We have seen that colloids prepared by any method are more or less unstable. The degree of instability, however, varies greatly from colloid to colloid, and for the same colloid varies with the method employed in preparing it. This is one roughly distinguishing feature between colloidal solutions and true solutions. The latter are in general perfectly stable and would persist indefinitely; the former are in a state of metastability.

Perhaps the most unstable of the colloids are the metals, especially if these are prepared by the Bredig method. They degenerate rapidly, the metal clotting and settling to the bottom. If these systems are warmed, the clotting takes place still more rapidly — and at once if an electrolyte is added.

On the other hand there are many sols, such as ferric hydroxide, which are relatively stable and will persist for a long time.

The precipitation of colloids by electrolytes is usually an irreversible phenomenon. The colloid particles clot and form a precipitate and this persists, not going back again into the colloid state. There are, however, exceptions to this general relation. It has been found that when gold from a gold sol was deposited by cataphoresis, it readily passed back again into the water reproducing the original, homogeneous sol. A similar observation was made by Linder and Picton[1] in connection with a sol of arsenic trisulphide. One part was concentrated by cataphoresis and the whole then allowed to stand. The colloid diffused back into the liquid and re-established homogeneity.

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[1] *Journ. Chem. Soc.*, **61**, 160 (1892).

Again, certain colloids which have been precipitated can be restored to the colloid condition simply by treating the precipitates with certain chemical reagents. Thus, Whitney and Blake[1] found that precipitated gold could be returned to the colloid condition by simply treating it with ammonia. Linder and Picton[2] found that if colloidal ferric hydroxide had been precipitated by a salt like sodium chloride, it was only necessary to remove the salt by careful washing in order to obtain the hydroxide again in the colloidal condition. Precipitated arsenic trisulphide was restored to the colloidal condition simply by treatment with hydrogen sulphide.

Action of Electrolytes on Colloidal Suspensions. — The action of electrolytes, and the non-activity of non-electrolytes, on suspensions can be shown qualitatively in the following way. Treat an aqueous solution of arsenic chloride with an aqueous solution of hydrogen sulphide, arsenic sulphide will be precipitated. On the other hand, treat an aqueous solution of arsenic trioxide with an aqueous solution of hydrogen sulphide and no precipitate is formed; the system simply acquiring a yellowish brown color. Why this difference?

In the first case the reaction proceeds thus —

$$2\,AsCl_3 + 3H_2S = As_2S_3 + 3HCl.$$

In the second case thus —

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O.$$

What is the difference?

In the first case an electrolyte — hydrochloric acid — is formed, which in the presence of water dissociates into ions. In the second case no electrolyte is formed; and we shall see that this is often the determining factor — the presence or absence of ions or charged parts determining whether we get a precipitate or a colloidal suspension. If this is true, when we add aqueous solutions of an acid, base, or salt, all of which contain ions, to the colloid of arsenic trisulphide formed, as described above, from arsenic trioxide, the sulphide of arsenic should be precipitated. Such is the fact. Conversely, the addition of non-electrolytes such as alcohol, cane sugar, etc. to the arsenic sulphide sol should not produce any precipitation, and such again is the fact. This would make it appear probable that *ions or charged parts* are the prime factors in determining and conditioning the precipitation of colloids. Why this is the case will be seen later.

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[1] *Journ. Amer. Chem. Soc.*, **26,** 1341 (1904).

[2] *Journ. Chem., Soc.*, **61,** 114 (1892); **87,** 1924 (1905.)

Microscopic and Ultramicroscopic Observation of the Precipitation of Colloids. — Linder and Picton[1] have described the precipitation of a suspensoid by an electrolyte, as seen under the microscope. If the solution of the electrolyte is introduced on one side of the field, the precipitation or cloudiness progresses across the field. The solid particles at first show active Brownian movement, which, as the particles become larger, is less and less pronounced and finally entirely disappears; the solid particles settling down as a precipitate.

The phenomena observed under the ultramicroscope are quite as interesting. Take a sol in which the particles are all amicrons, or in a state of division which is so small that they cannot be seen as separate reflecting discs. If a very dilute solution of an electrolyte is added, the amicrons become submicrons which, on further addition of electrolyte, become microns, and finally precipitated particles. The Brownian movement, which in the submicromic state is very active, becomes less in the micromic, and entirely ceases when the precipitate proper forms. The introduction of very small amounts of electrolytes may not cause a precipitate to form. Enough must be added to cause the Brownian movements of the parts to cease. This amount, however, is not independent of conditions. The *rapidity with which the electrolyte is added* is a conditioning factor. The more slowly the electrolyte is introduced the less precipitation of the colloid; therefore, in comparing the amounts of electrolytes that are necessary and sufficient to effect complete precipitation, we must define the conditions under which the precipitation is to be effected.

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[1] *Journ. Chem. Soc.*, 87, 1906 (1905).

Cause of the Precipitation. — Before taking up the results that have been obtained, let us raise and, if possible, answer the question, why do electrolytes precipitate colloidal particles? This raises the further question, why do the colloidal particles remain in a state of suspension and not form a precipitate? And this in turn raises the question still more fundamental for chemistry, is a precipitate or the colloidal state the natural condition of a solid formed as the result of a chemical reaction between two or more substances in solution?

Two substances such as sulphuric acid and barium chloride react molecule for molecule in the sense of the following equation:

$$H_2SO_4 + BaCl_2 = 2HCl + BaSO_4$$

The solid barium sulphate when first formed must be either in the molecular condition, or at most only a few molecules are aggregated. This is true in general of the formation of solids from two or more substances in solution. The clotting or precipitation is a secondary phenomenon, the primary condition of the solid being a suspension in the liquid or the colloidal state. We are so accustomed in qualitative and quantitative analysis to deal with precipitates that we are liable to look upon them as the condition to be naturally expected when a solid is formed; while just the opposite is the case.

Why a Colloid is Unstable. — Why does the solid not remain in the colloidal or suspended condition?

We have seen that the particles in a suspensoid are in general charged with electricity, and all of the particles in any given suspensoid are charged with the same kind of electricity. In some suspensoids all of the particles are charged positively, and in others all of the particles are charged negatively. In either case, since all of the particles in any given suspensoid have charges of the same sign, these naturally repel one another, and this would tend to keep the particles apart and prevent the formation of a clot or precipitate. Acting counter to this is the surface-tension between the solid particles and the liquid. The action of surface-tension is always to draw the object up into the smallest volume for a given mass. This is why mercury thrown upon a wooden table approaches the form of little spheres — the sphere having the smallest surface for a given volume. So with suspended particles, surface-tension acts to diminish the surface for a given volume, which tends to draw the small colloidal particles together into larger particles which are the units of clots or precipitates.

We have then these two forces acting counter to one another; and, keeping this fact in mind, we can understand the action of electrolytes in causing precipitation.

Colloidal solutions are exposed more and more to the air, which contains a large number of electrolytes. These are taken up in larger or smaller quantities and effect precipitation of the colloidal particles. This accounts in part for the instability of colloidal suspensions.

How Electrolytes Act. — Take a suspensoid in which all of the particles are charged positively. The water must then be charged negatively. Add an electrolyte, *i.e.*, a substance which in the presence of water dissociates into positively charged cations and negatively charged anions. The positively charged colloidal particles attract electrostatically the anions of the electrolyte, and the charges on the particles are thus, as it were, neutralized. Surface-tension can then draw these particles together and form a precipitate.

It is well known that under such conditions some of the electrolyte is usually carried down with the precipitate, and cannot be washed out of it. This is no doubt due, in part, to the fact that the electrostatic attraction between the positive colloid and the anion of the electrolyte holds the two so firmly together that they cannot be separated mechanically.

If the colloidal particles are charged negatively, exactly the reverse of what is described above occurs. The negative particles attract the cations of the electrolyte, and the remainder of the process is as described.

This theory of the precipitation of colloids by electrolytes we owe primarily to Burton.[1] Let us now see what experimental evidence there is bearing upon it.

Precipitation and the Valency of the Ion with Opposite Charge. — If the above conclusion is correct, if precipitation is due to the electrical neutralization of the charged colloidal particle by the ion with the opposite charge, then there ought to be a simple relation between the numbers of charges on the precipitating ions and the amounts of these ions required to effect the precipitation — a relation between the precipitation quantities of the ions and their valences. Freundlich[2] has carried out an elaborate series of experiments to test this point. If the sol is positive the valence of the anion carrying a negative charge is the conditioning factor.

Precipitation of a Positive Sol. — Take the positive sol, ferric hydroxide, containing 16.3 millimols to the liter. The following are the concentrations of the electrolytes just necessary to produce complete precipitation of the sol in a given time (two hours); all other conditions, such as the relation of the volume of the electrolyte to that of the sol, being kept constant.

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[1] *Phil. Mag.*, **12**, 472 (1906).

[2] *Zeit. phys. Chem.*, **44**, 129 (1903); *Kapillarchemie*, p. 352.

Electrolyte	Millimols in liter
$\overset{+}{K}, \overset{-}{Cl}$	9.03
$\overset{+}{K}, \overset{-}{Br}$	12.5
$\overset{+}{K}, \overset{-}{I}$	16.2
$\overset{+}{K}, \overset{-}{NO_3}$	11.9
$\overset{+}{Na}, \overset{-}{Cl}$	9.25
$\frac{\overset{++}{Ba}, \overset{--}{Cl_2}}{2}$	9.64
$\overset{++}{K_2}, \overset{=}{SO_4}$	0.204
$\overset{++}{Tl_2}, \overset{=}{SO_4}$	0.219
$\overset{++}{Mg}, \overset{=}{SO_4}$	0.217

It thus requires about the same amounts of the univalent anions to effect the precipitation, regardless of the nature of the cations with which they were combined in the compound.

When we turn to the bivalent anions very different amounts were required, but practically the same amounts regardless of the nature of the cations combined with them before the substance was dissolved and dissociated.

Precipitation of a Negative Sol. — Let us turn now to negative sols, such as the trisulphide of arsenic. Treat this with cations of different valences, and see how much of each is required to effect complete precipitation of the sol. Freundlich carried out these experiments with a sol containing 7.539 millimols to the liter. The number of millimols of each electrolyte is given in the table on the opposite page.

The results with negative sols are as satisfactory as with positive. About the same quantities of univalent cations are required to precipitate the negative sol. That larger quantities of potassium formate and potassium acetate are required than of potassium chloride or nitrate is probably due, in part, to the fact that formic acid is less dissociated than hydrochloric or nitric acids, and acetic acid still less than formic. The salts of these weaker

Electrolyte	Millimols in liter
$\overset{+}{\mathrm{K}}, \overset{-}{\mathrm{Cl}}$	49.5
$\overset{+}{\mathrm{K}}, \overset{-}{\mathrm{NO_3}}$	50.0
$\overset{+}{\mathrm{K}}, \overset{-}{\mathrm{HCOO}}$	86.0
$\overset{+}{\mathrm{K}}, \overset{-}{\mathrm{CH_3COO}}$	110.0
$\overset{+}{\mathrm{Na}}, \overset{-}{\mathrm{Cl}}$	51.0
$\overset{+}{\mathrm{Li}}, \overset{-}{\mathrm{Cl}}$	58.4
$\overset{++}{\mathrm{Mg}}, \overset{--}{\mathrm{Cl_2}}$	0.717
$\overset{++}{\mathrm{Mg}}, \overset{--}{\mathrm{SO_4}}$	0.810
$\overset{++}{\mathrm{Ca}}, \overset{--}{\mathrm{Cl_2}}$	0.649
$\overset{++}{\mathrm{Sr}}, \overset{--}{\mathrm{Cl_2}}$	0.635
$\overset{++}{\mathrm{Ba}}, \overset{--}{\mathrm{Cl_2}}$	0.691
$\overset{++}{\mathrm{Ba}}, \overset{--}{\mathrm{(NO_3)_2}}$	0.687
$\overset{++}{\mathrm{Zn}}, \overset{--}{\mathrm{Cl_2}}$	0.685
$\overset{+++}{\mathrm{Al}}, \overset{---}{\mathrm{Cl_3}}$	0.093
$\overset{+++}{\mathrm{Al}}, \overset{---}{\mathrm{(NO_3)_3}}$	0.095

acids are less dissociated than the salts of the stronger; and consequently, greater concentrations of the solutions are required to produce a given number of cations. The fact that more of the acetate is required than of the formate is in keeping with this view; acetic acid being weaker than formic, potassium acetate is less dissociated for a given concentration than potassium formate.

When we turn to the bivalent cations we find very much smaller amounts required to effect complete precipitation than with the univalent cations. Here again the amounts of the different bivalent cations required to effect the precipitation are of the same order of magnitude.

Very much less of the trivalent cation aluminium is required than of the bivalent cations. Practically the same amounts are necessary whether in the salt they were combined with the chlorine or with the $\overset{-}{\mathrm{NO_3}}$ ion.

Here again the same general relation comes out as in the positive sol. The amount of the ion with opposite sign required to effect complete precipitation is independent of the nature of the ion with the opposite sign, and dependent primarily on the valence of the "active" ion, or the number of electrical charges which it carries.

Take one further example, the precipitation of the negative platinum sol containing 0.7 milliatoms to the liter.

Electrolyte	Millimols in liter
$\overset{+}{\text{Na}}, \overset{-}{\text{Cl}}$	2.5
$\overset{+}{\text{K}}, \overset{-}{\text{Cl}}$	2.2
$\overset{++}{\text{Ba}}, \overset{--}{\text{Cl}_2}$	0.058
$(\overset{++}{\text{UO}_2}, \overset{--}{\text{NO}_3})_2$	0.065
$\dfrac{\overset{+++}{\text{Al}_2}, \overset{---}{(\text{SO}_4)_3}}{2}$	0.013

The same relations manifest themselves here again. For cations of the same valence essentially the same amounts are required. The amount of any cation necessary to effect complete precipitation is primarily a function of its valence.

Precipitation Not Proportional to Valence. — If we examine the above results quantitatively, we will find that while less of bivalent ions than of univalent, and of trivalent than bivalent, are necessary to effect the precipitations, the different amounts are not proportional to their valences; *i.e.*, it does not require half as much bivalent as univalent, and one-third as much trivalent as univalent ions to effect complete precipitation. The question is, why do these relations not hold quantitatively?

One other important factor must be taken into account. In order that the cation or anion may neutralize the charge on the colloidal particle it must be *adsorbed*. We have already seen that when colloidal particles are precipitated by electrolytes, some of the electrolyte is carried down in the precipitate and cannot be removed by any amount of washing. This electrolyte is undoubtedly adsorbed by the colloid.

If the colloid containing adsorbed electrolyte is treated with a solution of another electrolyte, the original cations can be replaced by those of the second electrolyte, which are similarly adsorbed by the colloid.

The different ions are adsorbed with different ease, and this explains in part why the precipitating quantities of the ions with different valences are not proportional to their valences.

We have thus far fixed our attention entirely on the ion of the precipitating electrolyte, which has an electrical charge opposite to that on the colloidal particle. A moment's thought will show that we cannot ignore the ion of the electrolyte having the same charge as the colloid. This often has the effect of rendering the colloid more stable. Thus, the hydrogen ion renders positive sols more stable, while the hydroxyl ion increases the stability of negative sols. In the cases of salts, the ion with the same charge as the sol tends to render the sol more stable, but this effect is so small in comparison with the precipitating action of the ion of opposite sign, that the effect of the valency of the latter is not completely marked.

Taking all of these factors into account, adsorption, protecting effect of the ion with the same sign, etc., we can see why the quantities of the ions of different valence which are necessary to effect complete precipitation are not proportional to their valences, and yet the explanation of precipitation already considered may be perfectly valid.

Precipitation of Coarser Suspensions by Electrolytes.— The action of electrolytes on coarse suspensions is strikingly analogous to their action on the finer suspensions. Take a coarse suspension of sulphur. It is charged negatively and precipitated by sodium, potassium and ammonium chlorides, sulphates, etc., having a concentration of from 0.1 to 0.6 molecules in a liter. Magnesium, calcium and barium chlorides effect the precipitation in concentrations ranging from 0.01 to 0.02 molecules per liter. Here the same relation manifests itself between the valence of the ion with charge opposite to that on the colloid and its precipitating power, as with the finer or more dispersed suspensions. This relation then seems to be general, regardless of the dispersity of the suspensoid.

Precipitation of Emulsoids by Electrolytes. — Much less is known about the action of salts on emulsoids than on suspensoids, and the phenomena seem to be more complex and less amenable to generalization. The interesting and important relations which we have just been considering with suspensoids, fail to manifest themselves with the emulsoids. This may be due in part to the fact that the emulsoids occupy a position intermediate between suspensoids and true solutions, probably owing to their relatively high dispersity.

The facts that have been brought out in connection with the precipitation of emulsoids by electrolytes are almost wholly empirical, and will therefore be very briefly discussed.

The precipitation of suspensoids is sometimes a reversible, and sometimes an irreversible process. Under certain conditions the precipitate will pass back into the colloidal state; under others it remains a precipitate.

When emulsoids are precipitated by the addition of salts, the process is sometimes reversible, the precipitate passing back into solution on the addition of more water.

The effect of salts on *gelatine* is in general to cause it to precipitate if the concentration of the salt solutions is sufficiently great. This process is irreversible and thus differs from another transformation in the case of gelatine which is reversible and of far greater interest. This is the transformation of the sol to the gel, and of the gel to the sol. *Gelation* is effected by simply allowing a concentrated solution of gelatine obtained at a higher temperature, to cool. The reverse process, or *solation,* is effected simply by warming the gel.

The precipitation of *albumin* by some salts is for a time a reversible phenomenon, by others non-reversible from the beginning. The reversible transformation becomes non-reversible on standing. Small amounts of the heavy metals are sufficient to precipitate albumin, while concentrated solutions of salts of the alkalies and alkaline earths are required.

No relations of value, or even of interest, have been discovered in connection with the precipitation of emulsions by salts. The power of a salt to precipitate a suspension is, as we have seen, a function of the valency of the ion of the salt having a charge opposite in sign to that on the colloid. No such relation manifests itself with emulsions. The valency of the precipitating ions seem to have nothing to do with the phenomenon.

Precipitating Action of one Colloid on Another.—Neisser and Friedemann,[1] and Biltz[2] found that suspensoids with like electrical charges do not, when mixed, have any appreciable effect on one another. Suspensoids *with opposite electrical charges, however, precipitate one another.* This is just what would be expected from the action of electrolytes on suspensions. The ions having a charge opposite to that on the colloid are the conditioning factors in the precipitation of suspensions by electrolytes.

Thus, when the positive sols, aluminium, iron, chromium, etc., hydroxides, are added to the negative sols, arsenic, antimony, cadmium, etc., sulphides, both sols are more or less precipitated; the amount of each that is precipitated depending on the relative amounts of the two sols present. If negative sols are added to negative, or positive to positive, there is no precipitation.

When we were studying the precipitation of colloids by electrolytes, we saw that the amount of the precipitation was conditioned not only by the amount of the electrolyte added to the colloid, but also by the way in which it was added, whether all at once, or slowly, a drop at a time. The same relation obtains for the precipitation of a colloid by one of opposite sign. If the one sol is added quickly to the other there is a different amount of precipitation than if the two sols are mixed a little at a time.

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[1] *Münch. Med. Wochenschrift,* No. 11 (1903).

[2] *Ber. d. chem. Gesell,* **37,** 1095 (1904.)

The amount of precipitation of a sol by one of opposite sign is conditioned fundamentally by the amount of the one that is added to a given amount of the other. This is shown by the following data for colloidal antimony trisulphide to which colloidal ferric hydroxide was added. To 2 cubic centimeters of the antimony trisulphide sol, containing 5.6 milligrams, the ferric hydroxide sol was added.[1]

Milligrams Fe_2O_3	Result directly after mixing	Result after one hour
0.8	Cloudy	Nearly homogeneous
3.2	Small flakes	Unchanged
4.8	Flakes	Liquid yellow
6.4	Complete precipitation	Complete precipitation
8.0	Slow precipitation	Complete precipitation
12.8	Cloudy	Slight precipitation
20.8	Cloudy	Homogeneous

A small amount of the ferric hydroxide produces little or no precipitation. More produces complete precipitation, while a much larger quantity produces little or none.

There is an amount of one sol which is just equivalent to another, and which will just precipitate it. This has been found to be the case when the two sols are present in electrically equivalent quantities.

The reason why large amounts of the one sol do not completely precipitate the other, is probably that the particles which are present in large excess surround those present in smaller quantity and practically eliminate them from the field of action.

Michaelis and Pincussohn[2] studied the action of one sol on another with different sign, under the ultra-microscope. They used sols in which the particles had different colors, and observed that the number of each became smaller and smaller, and therefore they must have united with one another.

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[1] *Biltz, Ber. d. chem. Gesell.*, **37**, 1106 (1904).

[2] *Biochem. Zeit.*, **2**, 251 (1906–1907).

Action of Emulsoid on Emulsoid. — We have seen that when emulsions are treated with electrolytes, the phenomena are not so simple or so clean cut as when these same substances act on suspensions. The same holds true when one emulsion is treated with another. In the first place, the emulsions are not charged positively and negatively in the same clean-cut manner as suspensions. Positive emulsions will often precipitate negative emulsions, but the quantitative relations that obtain with suspensions are lacking here. Emulsions are more like true solutions than suspensions, are more readily adsorbed, and are more capable of entering into chemical reaction with one another. The phenomena here, as a whole, are more complex, and no general relations have thus far been established.

Action of Suspensions on Emulsions. — When the two types of colloids having opposite signs are mixed in certain proportions, a precipitation results. If they are mixed in other proportions they exert a protective action on one another. No general relations have been established.

Protective Action of Colloids. —Lottermoser and von Meyer[1] noted that albumin protects silver sols from precipitation by electrolytes while Zsigmondy[2] studied the action of various sols on colloidal gold. The latter took a certain amount of a solution of colloidal gold and added varying amounts of emulsions and 1 cubic centimeter of a two-normal solution of sodium chloride. He determined the amount of the emulsion which just prevented the change of the red gold into blue. This expressed in milligrams he termed the "*gold number.*" A few of Zsigmondy's results are given in the table on the following page.

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[1] *Journ. prakt. Chem.*, **56**, 242 (1897).

[2] *Zeit. anal. Chem.*, **40**, 697 (1901).

Emulsion added	Gold number
Gelatine	0.005 – 0.01
Casein	0.01
Egg albumin	0.1 – 0.2
Gum arabic	0.15 – 0.25
Dextrin	10 – 20
Potato starch	25
Sodium stearate	10 (at 60°); 0.001 (at 100°)
Sodium oleate	0.4 – 1

Colloidal solutions of the sulphides are protected as well as the colloidal metals; and silicic acid as well as the organic colloids exerts a protecting influence on the metal sols.

It may be said in general that when a suspension is added to an emulsion, the system has the properties of the emulsion. This has been explained by Bechhold as due to the emulsion forming a coating around the suspension and giving its characteristic properties to the suspension.

GELS

According to Freundlich[1] a gel is a two-phase system in which the dispersing agent is a solid, and the dispersed phase a liquid. Gels are frequently formed when emulsoids are concentrated by evaporation. They consist of thin walls of the amorphous solid surrounding a space filled with liquid. The structure of gels has been studied microscopically by Bütschli,[2] in the cases of gelatine, albumin, cellulose, starch, etc. It is so fine that the highest magnification must be employed.

The study of gels is extremely difficult, and knowledge of them has been accumulated but slowly. They are very complex, do not lend themselves to the ordinary methods of investigation, are very sensitive to the influences of foreign substances, to changes in temperature, etc. Some progress has been made, however, in the study of gels; especially in the study of the sol-gel transformation, solvation and desolvation of gels, and the transformation of the amorphous solid into a crystalline solid.

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[1] *Kapillarchemie*, p. 474.

[2] *Verh. Naturwiss. Med. Vereins*, Heidelberg, N. F., **5**, 89, 230, 360 (1893—1894); **6**, 287 (1900).

Physical Properties of Gels. — Barus[1] has shown that gels are far more compressible than solids, the compressibility increasing with the temperature. When a gel is treated with water the resulting *volume* is less than the sum of the volumes of the two. The *density* is determined by these volume relations.

It is well known that the *viscosities* of gels are a function of their concentrations, the viscosity increasing rapidly with the concentration.

The *diffusion* of substances in gels is not very different from diffusion in pure water, provided the gel is not too concentrated. If the gels are very concentrated, diffusion of salts through them is very much slower than through pure water.

These facts may be explained as follows, if we consider the structure of gels to be that of a honeycomb, or lattice work. In a dilute gel the concentration of the solution in the open spaces (Hohlräumen) is approximately the same as that in the outer liquid; and the gel walls offer little resistance to the passage of the dissolved substance. Hence the rate of diffusion is nearly the same as that in pure water. In concentrated gels, however, the gel walls offer decided resistance to the passage of the dissolved substance; and hence, although the diffusion really takes place in the gelatine-poor liquid in the open spaces (Hohlräumen), the rate of diffusion is considerably diminished.

The *expansion* of the gel with rise in temperature is of the same order of magnitude as the expansion of the liquid component of the gel.

It is well known that glass and many other substances, when subjected to pressure, show double refraction. The properties of glass show it to be a very viscous liquid cooled below its true freezing-point. The question arises whether other viscous liquids subjected to mechanical strain would not show similar properties. Such has been found to be the case with collodion, gelatine, etc.

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[1] *Amer. Journ. Science*, **6**, 285 (1898).

Solventation and Desolventation of Gels. — It is well known that gels have the power of taking up and of giving up liquids. This process may or may not be analogous to the hydration and dehydration of molecules and ions in the presence of water. To distinguish it from the latter, it seems better not to use the terms hydration and dehydration in water, and solvation and desolvation in solvents in general; but to employ such distinguishing words as solventation and desolventation. This subject will be discussed as Freundlich[1] has done under the two heads: the less elastic and the more elastic gels.

Less Elastic Gels. — The study of these systems we owe almost entirely to Van Bemmelen.[2] He studied the hydrates formed by such substances as aluminium and iron oxides, to see whether they corresponded to definite chemical compounds. It was found that in a desiccating atmosphere such systems lose water perfectly *continuously*, and take it up from air containing much water in the same manner.

A definite hydrate in the presence of its own decomposition products has a definite vapor-tension, and this remains practically constant as long as there is any of this hydrate present. Such is not the case with these gels. As the water is removed, the vapor-tension *gradually* becomes less and less with increase in concentration, as in the case of a true solution.

The hydration and dehydration of silicic acid has been studied in much detail. The dehydration curve is for the most part continuous, but in places is nearly parallel with one of the axes, showing that over this region there is loss of water without any considerable change in vapor-pressure. The opalescent appearance in this region suggests a change in the dispersity, which is also indicated by a change in the color.

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[1] *Kapillarchemie,* p. 486 (1909).

[2] *Ber. d. chem. Gesell.,* **11,** 2228 (1878); *Zeit. anorg. Chem.,* **5,** 466 (1894); **13,** 233 (1897); **18,** 14, 98 (1898); **30,** 265 (1902).

The hydration curve in part follows the dehydration curve, but in places differs markedly from it. The changes in dispersity, opalescence and color, the reverse of those in dehydration, manifest themselves.

It has been found that the previous history of the gel, or its *hysteresis*, determines its properties.

More Elastic Gels. — The class of the more elastic gels includes especially such compounds of carbon as albumin, starch, agar-agar, etc. The swelling or imbibition of these substances with water are matters of physiological importance. The amount of water which can be taken up by gelatine is very large indeed. Thus, Von Schröder[1] has found that a plate of gelatine weighing 0.904 grams, when exposed for eight days to an atmosphere saturated with water-vapor, will take up 0.37 grams of water. When exposed for twenty days under the same conditions, the weight does not further change. The water thus taken up can be removed by placing the plate in a dry atmosphere.

If the plate containing all the water which it can absorb from the atmosphere, is plunged into water, it will absorb a *far larger quantity of water*. It was found that the plate mentioned above, weighing 1.27 grams, would, at room temperature, take up in an hour 5.63 grams of water. If such a plate is allowed to remain in water for a day or so, it will take up a maximum amount of water, and this will not still further increase. There seems, under these different conditions, to be a kind of equilibrium between the plate and the water-vapor on the one hand, and liquid water on the other.

The volume of the gel alone, in taking up water, is greatly increased. Lüdeking[2] has shown, however, that when a gel has taken up water, the volume is less than the sum of the volumes of the dry gel plus the water.

The *pressure* which gels will produce when they absorb water cannot be measured directly, since the volume of the gel which has taken up water is less than the sum of the volumes of the dry gel and the water. Von Schröder[1] used unglazed porcelain cells through which water would pass, but the gel could not. These played the rôle of the semipermeable membranes in the measurements of osmotic pressure. The water passed into the cell, was taken up by the gel and the resulting pressure was great enough to cause the cell to break. Roughly quantitative measurements of these pressures were made by Reinke,[2] who worked out also the moduli of elasticity of imbibition when different amounts of water had been taken up.

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[1] *Zeit. phys. Chem.*.**45**, 75 (1903),

[2] *Wied. Ann.*, **35**, 552 (1888).

Some idea can be gained of the pressure produced by imbibition by taking gels which have imbibed water and drying them in contact with thin plates of such solids as glass. Cover a glass plate with a thin layer of gelatine which has taken up water. Place the whole system in a desiccator and dry the gel. The glass plate will be strongly bent, and may even be broken. This explains the observation made by Cailletet,[3] that glass plates on which a film of gelatine is allowed to dry, show double refraction. This is, of course, due to the strain produced by the drying gel.

Rate at Which Water is Taken Up. — The rate at which the water is taken up by gels was studied by Hofmeister,[4] who found that the water was at first taken up very rapidly, and then more and more slowly. This is shown by the following results.

PLATE OF AGAR 0.395 MM. THICK

Time in minutes	Grams water imbibed
5	2.52
10	3.02
15	3.37
20	3.54
25	3.73
30	3.89

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[1] *Zeit. phys. Chem.*, **45,** 75 (1903).

[2] *Hansteins botan. Abhandl.*, **4,** 1 (1879).

[3] *Compt. Rend.*, **134,** 400 (1902).

[4] *Archiv. exp. Pathol. u. Pharmakol,* **27,** 395 (1890).

Similar results were obtained by Reinke.[1]

The Effect of Temperature on the Rate of Imbibition is a Matter of Importance in Living Things. — It has been studied by Dimitrievics,[2] and by Reinke.[3] In one case investigated, after six hours at 5° the imbibition was 60 percent of the maximum; at 35° it was 97 percent of the maximum. The total amount of water taken up or the imbibition maximum in the two cases was, however, essentially the same, the equilibrium being practically unchanged by temperature. Nevertheless, the equilibrium was reached at the higher temperature in 24 hours, while 48 hours were required at the lower temperature.

Heat Set Free in Imbibition. — The heat that is liberated when imbibition takes place is a matter of the very greatest importance in understanding the nature of this process, and will prove to be fundamental to the application of thermodynamics to such processes when enough is known about them to enable them to be treated by mathematical procedures. The first to make quantitative measurements of the heat liberated in imbibition were Wiedemann and Lüdeking.[4] Some of the best results were obtained by Rodewald.[5] A few of his data are given below.

100 grams dry starch % water	Heat in calories evolved per gram starch
0.23	28.11
2.39	22.60
6.27	15.17
11.65	8.43
15.68	5.21
19.52	2.91

Most of the heat is liberated in the imbibition of the first amounts of water. This conclusion was confirmed by the extended investigations of Rodewald and Kattein[6] on a large number of kinds of starch. This is strictly in keeping with the fact that high temperatures are necessary to remove the last traces of water from gels.

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[1] *Hanst. bot. Abhandl.*, 4, 42 (1879).

[2] *Wissenschaft. prakt. Unters. d. Gebiet Pflanzenbaues*, I, 75.

[3] *Hanst. bot. Abhandl.*, 4, 83 (1879).

[4] *Wied. Ann.*, **25**, 145 (1885).

[5] *Zeit. phys. Chem.*, **24**, 206 (1897).

[6] *Ibid.*, **33**, 586 (1900).

Before leaving the subject of imbibition, the fact should be mentioned that certain gels imbibe liquids other than water. Thus, caoutchouc imbibes carbon disulphide, ether, chloroform, etc.

Imbibiton in Aqueous Solutions. — As Freundlich[1] points out, imbibition in solution is of fundamental importance, because the imbibition of colloids is fundamental for living things, and the imbibition of colloids in nature takes place in solution.

When a gel is brought into the presence of a solution of a salt, the salt distributes itself between the gel and the solvent. In the presence of different salts imbibition by the colloid takes place with very different rapidity. Thus, Hofmeister[2] showed that the chlorides of ammonium, sodium and potassium, and the nitrate and bromide of sodium, accelerate the velocity of imbibition; while the nitrate, sulphate, tartrate, etc., of sodium and the polyhydroxyl organic compounds retard imbibition.

Wenzel[3] found that the sulphocyanate ion greatly accelerates the rate of imbibition, while Wo. Ostwald found that whatever favors gelation retards imbibition.

Hofmeister[4] has also shown that adsorption plays a prominent rôle in imbibition. Thus, the dye-stuff methylviolet is strongly adsorbed by gelatine.

THEORIES OF THE COLLOIDAL STATE

Are Colloids Solutions? — The first question that suggests itself is, are colloids true solutions? To the eye, many of them appear to be true solutions. The systems seem to be homogeneous, and the ordinary microscope often fails to reveal any heterogeneity, as has been stated. They have some of the properties of true solutions —

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[1] *Kapillarchemie,* p. 512 (1909).

[2] *Arch. exp. Pathol. und Pharmakol.*, **28**, 210 (1891).

[3] *Quellkraft der Rhodanate, Gera* (1886).

[4] *loc. cit.*

osmotic pressure causing diffusion, lowering of freezing-point, lowering of vapor-tension; but they have these properties to only a very slight extent. True solutions show osmotic pressures which obey the laws of gas pressure. Substances in true solution lower the freezing-points and the boiling-points of solvents in terms of Raoult's laws.

Certain investigators have attempted to use these properties of colloids to determine the molecular weights of the colloidal particles, just as we use them with true solutions to determine the molecular weights of dissolved substances. Gladstone and Hibbert have applied the freezing-point and the boiling-point methods to the determination of the molecular weights of such colloids as caramel, gum, ferric hydroxide, etc. Sabanejew and Alexandrow determined by the freezing-point method the molecular weight of albumin to be about 15,000.

Sabanejew distinguished between colloids with smaller molecular weights, *i.e.*, less than 30,000; and those which gave no appreciable lowering of the freezing-point, and which were therefore assumed to have very great molecular weights, at least greater than 30,000. These include such substances as ferric hydroxide, starch, silicic acid and the like. The large molecules or particles of colloids are, of course, made up of aggregates of smaller molecules. Looking at the solution theory of colloids in a broad way, we may say that it is *not sufficient.* Many properties of true solutions are either not present in colloidal solutions at all, or are present to only a slight extent; and, conversely, colloidal solutions have many properties not found in true solutions. The determinations of the molecular weights of colloids referred to above, all assume that Raoult's laws for lowering of freezing-point and lowering of vapor-tension hold for colloidal solutions. This is a pure assumption, and a highly improbable one. Therefore, in assigning a number to the molecular weight of any colloidal particle, we must remember that it probably bears no very close relation to the facts, and what that relation is we at present do not know, and have no means of finding out.

The Adsorption Theory of Colloids. — We have already seen that adsorption plays a prominent rôle in colloid chemistry. Certain colloids adsorb certain dye-stuffs, and when colloids are precipitated by electrolytes, some of the electrolyte is carried down with the precipitate and adheres so firmly to it that it cannot be removed by washing. This all suggests adsorption phenomena. It is further obvious that the colloidal particles, being so small, have very large surfaces, and adsorption phenomena are, as we have seen, surface phenomena. That adsorption must be taken into account in dealing with colloids is quite certain, but this alone seems insufficient to explain the nature of colloidal solutions.

The Suspension Theory of Colloids. — The prevailing theory of colloids today, is that they are simply suspensions of finely divided parts in the liquids. This theory is in accord with the microscopic and ultramicroscopic study of colloidal solutions. The coarser suspensions can be seen with the microscope, the finer with the ultramicroscope. In some colloidal solutions the particles are so fine that they cannot be seen even with the ultramicroscope.

Linder and Picton carried out the following experiment bearing on the suspension theory of colloids. They filtered colloids under pressure through porous porcelain. Some were filtered out completely by the porcelain, while others were so fine-grained that they passed on through. Thus, the coarser suspensions were separated from the finer. In terms, then, of the suspension theory, the colloidal particles are simply in a state of mechanical suspension in the liquid; the properties of the colloid being primarily a function of the size of the colloidal particles. In the suspensions the particles are larger than in the hydrosols, and the latter therefore resemble the true solutions more closely in their properties.

It should be pointed out, however, that the electrical properties of certain colloids cannot be satisfactorily explained in terms of the suspension theory alone. The movements of the colloidal particles toward the pole would indicate a slight solution and ionization of the colloid. It is easier to explain the precipitation of one colloid by another having the opposite charge, on the theory that there is slight solution of the colloidal particles. It would thus seem that the suspension theory of colloids must be supplemented by the solution theory to some extent, and at least in some cases, in order to interpret the phenomena presented by colloids.

A number of modifications of the suspension theory of colloids have been recently proposed by the leading workers in this field. One supplementary theory will be referred to.

What is the condition of the suspended colloidal particles? Von Weimarn[1] studied the precipitate formed by bringing together solutions of certain concentrations. He found that they were crystalline. When the solutions were more dilute or more concentrated, the crystals were smaller and smaller, and finally could be seen only with the aid of the ultramicroscope. It therefore seems probable, thinks Von Weimarn, that when very dilute solutions are brought together and form a colloid, the colloidal particles are also crystalline.

Just as extrapolation beyond the facts is in general a dangerous physical process, so here it seems a dangerous procedure to conclude from the crystalline nature of precipitates, that the much finer-grained colloidal particles are also crystalline. They may be crystalline, or they may not be crystalline; this remains to be proved.

Bearing of Colloid Chemistry on other Branches of Science

The bearing of colloids on living processes has already been referred to. This will now be discussed in some detail, since colloids are coming more and more to the front in dealing with biological processes.

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[1] *Koll. Zeit.*, **2**, 76 (1907).

Bearing of Colloids on Physiological Chemistry. — As early as 1858 the botanist Nägeli recognized that substances were present in plant cells in what he called "special" condition. This was before the colloidal condition of matter was known.

Light has been thrown on the passage of food-stuffs through the walls of plant cells. These walls are analogous to the membranes used by Graham for effecting dialysis. Through these substances, as Graham showed, crystalloids such as sugar can pass, but colloids, such as starch, albumin, etc., cannot pass.

Pauli[1] has studied albumin from the standpoint of colloidal chemistry; protoplasm being a very complex colloidal solution. Colloidal chemistry has played a prominent part in explaining the way in which food is supplied to living things. One or two well-known physiological processes will be considered in some detail.

Relations Between Organic and Inorganic Ferments. — The method devised by Bredig for preparing colloidal solutions of the metals has already been discussed. It consists in bringing two bars of the metal in question near together under water, and passing an electric current between the bars. Under these conditions the metal is torn off in a finely divided state, and remains in the water as a suspension.

Bredig and von Berneck,[2] when they described this method, published the results under the heading "Inorganic Ferments." Let us now see why they used this title.

Very minute traces of certain organic ferments decompose hydrogen dioxide at an appreciable rate. A colloidal suspension of platinum containing a gram-atomic weight (195.2 grams) in seventy million liters of water decomposes hydrogen dioxide slowly.

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[1] *Kolloidchemische Studien am Eiweiss*, Dresden (1908).

[2] *Zeit. phys. Chem.*, **31**, 258 (1899).

This relation between colloidal platinum and the organic ferments is, in itself, not so striking. There are many other substances which, in small quantities, decompose hydrogen dioxide. Superoxides in the finely divided condition decompose hydrogen peroxide.

One of the most striking relations between the colloidal metals and organic ferments is to be found in the action of certain "poisons" on both. Certain substances in very minute quantity, diminish very appreciably the rate at which they decompose hydrogen dioxide. If we arrange these poisons in the order of their poisonous property to organic ferments, and then arrange them with respect to their poisonous action on colloidal platinum, the two arrangements are practically identical.

It has been further proved that the action of the organic ferments is catalytic, *i.e.*, a little of the ferment effects a large amount of reaction, and the ferment does not itself enter into the reaction.

Bredig and von Berneck,[1] Ikeda[2] and Reinders[3] showed that colloidal solutions of gold, platinum, iridium, etc., are true catalyzers. We know that catalytic action is fundamentally a surface phenomenon; a catalyzer catalyzing the more, the larger its surface. We can now understand how it is that such minute traces of certain substances "poison" both the enzymes and the colloidal metals. Surface tension is greatly affected by small quantities of impurities. This is well recognized in all measurements of surface-tension. Minute traces of such substances as hydrocyanic acid, hydrogen sulphide, mercuric chloride, etc., probably exercise their poisonous property, by way of their effect on the surface-tension of the catalyzer.

The analogies between the organic ferments and the colloidal solutions of the metals are thus many and apparently deep-seated. This is another important relation between colloidal chemistry and physiological chemistry.

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[1] *Zeit. phys. Chem.*, **31**, 258 (1899).

[2] *Ibid.*, **37**, 1 (1901).

[3] *Ibid.*, **37**, 323 (1901).

Action of Toxins on Antitoxins. — Few questions in physiological chemistry have come more to the front in recent years, than the one dealing with the reaction between toxins and antitoxins. We recall especially the discussion between Erlich, on the one hand, and Arrhenius and Madsen on the other. The former would explain the reaction purely on the basis of structural chemistry. The latter would invoke the aid of physical chemistry. So far as colloidal chemistry plays a rôle in these reactions, the subject must be discussed in this place.

Arrhenius[1] studied the diffusion constants of certain toxins and antitoxins in gelatine. From the small values found he showed that both toxins and antitoxins are colloids, the antitoxin showing the colloidal nature even more pronounced than the toxin.

Madsen[2] and Biltz[3] studied the action of the antitoxin on the toxin of diphtheria, assuming that the phenomenon is primarily one of adsorption. On this assumption they calculated the amount of antitoxin to toxin, and then compared the results of calculation with those of experiment.

Free toxins in the solution	Toxins to antitoxin	
	Calculated	Observed
1.2	180	197
17.2	240	237
49.8	270	251
72.8	280	272

The relation between the values calculated and those found experimentally is as close as could be expected when we consider the nature of the phenomena in question.

Arrhenius[4] supposed that the action of an antitoxin on a toxin was a chemical reaction analogous to the action of an acid on a base. He deduced the equation for the equilibrium of a weak acid acting on a weak base, and attempted to apply it to the action of certain antitoxins on toxins. The constants calculated from the Arrhenius equation and those found experimentally are surprisingly close, which would point to the general correctness of the Arrhenius idea.

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[1] *Immunochemie,* p.17.

[2] *Ibid.,* p. 131.

[3] *Mediz. Naturwiss. Arch.,* **1,** 362 (1907).

[4] *Immunochemie,* Chapt. 3.

There is, however, one fact which seems to militate against the view of Arrhenius — the specific nature of the reaction between toxin and antitoxin. Höber and Gordon[1] have shown that the amount of a toxin which a given amount of its antitoxin will neutralize depends upon how *rapidly* the one is added to the other. Take the amount of antitoxin which, when added rapidly, is just sufficient to neutralize the toxin, and add it slowly; it will not neutralize all of the toxin, which is shown by the fact that the mixture is still strongly toxic.

This suggests the reactions between colloids with which we are now familiar, and would seem to place this reaction under the category of colloids. It is a little difficult to interpret this fact in terms of the view that the reaction between toxins and antitoxins is strictly analogous to the reaction between even weak acids and weak bases, which, in principle, is independent of the nature of both the acid and the base.

Both the chemical and the adsorption theories seem to have much in their favor, but at present we are not sufficiently conversant with the facts involved to enable us to decide between the two. It may be shown here, as in so many other cases, that both theories, which at present seem antagonistic, contain a part of the truth.

Bearing of Colloids on Pharmacology and Pathology. — Colloids are coming more and more to the front in pharmacology.[2] This is especially true where the colloids are very fine-grained and therefore approach more nearly to true solutions. The hydrosol of silver has valuable antiseptic properties, and the hydrosol of mercury has proved to be useful in dermatology; and only the beginning seems to have been made in the application of colloids to medicine.

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[1] *Beiträge chem. Physiol. u. Pathol.*, **5**, 436 (1904).

[2] *Porges, Kolloidchemie und Medicin, Koll. Zeit.*, **5**, 301 (1909).

Some glimpse of the bearing of colloids on pathology is given by the work of Fischers[1] on œdema. It was hitherto supposed that this is due to a rise in blood pressure, or to the walls of the vessels becoming less resistant. He has shown that œdema results if water is imbibed by certain colloids.

It is safe to predict that here again only a beginning has been made in the application of colloids to, and their bearing on, pathology.

Bearing of Colloids on Agricultural Chemistry. — It has been difficult, not to say impossible, to explain many of the processes which go on in the soil by physical and chemical means alone. Much valuable scientific work on the chemistry of soils, of fertilizers and of plant growth has recently been done. Colloidal chemistry has proved invaluable in interpreting the results that have been obtained.

There are present in the soil as colloids the hydroxides of silicon, iron and aluminium, and especially humus which plays such an important rôle in plant growth. Humus adsorbs phosphoric acid which is so essential to plant growth. The bases are adsorbed in the order potassium, sodium, calcium, and magnesium, potassium being the most adsorbed; and, of the common constituents of soils, sodium and calcium the least. When potassium salts are added to soils already saturated with sodium or calcium salts, the place of a part of the latter is taken by some of the former, which explains the tenacity with which soils hold their potash, which is so essential to the growth of such a large number of plants. This is another of those facts usually taken as a matter of course, or of chance, upon which the present economy of nature so vitally rests. The adsorption of the various constituents of fertilizers and of manures by the soils, and the imbibition of water in the soils, are probably directly connected with the presence of colloids in the soils.

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[1] *Das Odem: Eine experimentalle und theoretische Untersuchung der Physiologie und Pathologie der Wasserbindung in Organismen* (1910).

The question arises, whence came these colloids in the soils? The answer is, largely from the decomposition of the rocks.

Bearing of Colloids on Mineralogy. — Corun has shown that many minerals are really gels. Thus, opal, bauxite and many other minerals belong in this class. These gels are produced by the weathering of the rocks.

Colloidal chemistry has proved very useful in explaining the color of minerals. Rock salt is colored blue by the presence in it of colloidal sodium. When minerals and glass are subjected to the radiations from radium they become colored, due probably to the decomposing action of the radium — radiations liberating colloidal metal in the mineral or in the glass.

COLLOIDAL CHEMISTRY AND THE CHEMICAL INDUSTRIES

We have seen that the emulsoids occupy a position intermediate between true solutions and suspensoids. They have some of the properties of true solutions, but have these to a much less extent than true solutions; *i.e.*, osmotic pressure, lowering of freezing-point, lowering of vapor-tension. Their molecular weights, while large as compared with most truly dissolved substances, are still apparently much smaller than the weights of the suspended particles in true suspensions.

There are certain substances which seem to occupy positions intermediate between the emulsoids and true solutions, and these have been termed by Freundlich[1] and others *semi-colloids*. These substances have very great technical significance. They are also of physiological importance. When albumin is saponified it yields, according to Paal,[2] certain acids which have properties intermediate between true solutions and emulsoids. Their molecular weights are between 700 and 800, and they diffuse through parchment. They also have some colloidal properties, and are therefore classed as semi-colloids. Peptone also belongs in this class. It is an amphoteric electrolyte; its reactions show that some of its molecules are not only dissolved, but are ionized. Its molecular weight by the freezing-point method is between 300 and 500.

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[1] *Kapillarchemie*, 436 (1909).

[2] *Ber. d. chem. Gesell.*, 35, 2195 (1902).

Action of Soaps. — Soaps have been studied by Krafft[1] and co-workers, and they have found some remarkable relations between properties and concentrations. With increase in the concentration of the solution the boiling-point, instead of being raised, is actually lowered. The foamy nature of the solution rendered boiling-point determinations difficult and, in the more concentrated solutions, accurate determinations impossible. Smits[2] measured the lowering of the vapor-tension of water at 80° by sodium palmitate. A normal solution gave no lowering that could be measured, while a half-normal solution produced a lowering of 1.3 millimeters of mercury.

This would indicate that in the more concentrated solution we have to do almost entirely with colloids, while as the solution is diluted, these pass over more and more into semi-colloids and truly dissolved substances. As the dilution of the solution increases the alkali salts of the fatty acids are hydrolyzed by the large amount of water present into the free acids and the free bases, which dissolve and show the normal properties of solutions of electrolytes.

Krafft and Stern[3] have shown that free organic acids are present in solutions of soaps. When solutions of soaps of palmitic and stearic acids are warmed, the hydrolysis is increased and more of the acids is set free. These acids, being comparatively insoluble in water, exist as small droplets which produce a milky solution. The above-named investigators have shown that the acids can be extracted with toluene. While the soaps in aqueous solution show colloidal properties, in alcohol they form true solutions. Krafft[1] determined the molecular weights of a number of soaps in alcohol, using the boiling-point method, and found that they are in the simplest molecular condition.

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[1] *Ber. d. chem. Gesell.*, **27**, 1747 (1894); **28**, 2566 (1895); **29**, 1328 (1896); **32**, 1584 (1899).

[3] *Ber. d. chem. Gesell.*, **27**, 1752 (1894).

[2] *Zeit. phys. Chem.*, **45**, 608 (1903).

Tanning. — The process of tanning is also largely dependent upon colloids. The albumin of the skin takes up water, the amount depending upon the nature of the electrolyte present. In the presence of certain acids enormous amounts of water are thus taken up.

The gels of the skin undoubtedly adsorb sols from the tanning liquid, and the quality of the leather produced depends largely on the nature of the sols in the liquid. The more readily adsorbed colloids are deposited on the surface of the leather; the less readily adsorbed diffusing into the body of the leather. By suitable choice of tanning liquid, the skin is thus tanned to different depths.

Dyeing. — Another technical process in which colloids play a prominent rôle, is the art of dyeing. Many of the organic dye-stuffs are colloids, and many of the substances dyed exhibit the colloidal property of imbibition. Among the colloidal dyes[2] are such important substances as Congo red, Congo brown, benzo-purpurine, azoblue, aniline blue, etc.

On the other hand many of the dye-stuffs are true solutions, having large osmotic pressures and therefore showing true diffusion. By the boiling-point method they give normal molecular weights and under the ultramicroscope appear perfectly clear. To this class belong such important dyes as alizarine red, auramine, fluorescein, eosin, methylene blue, safranine, rhodamine, etc.

Lying intermediate between the dyes which are very colloidal and those which are true solutions, come certain dyes which have only some colloidal properties. These diffuse fairly rapidly, show considerable rise in boiling point, but under the ultramicroscope the suspended particles can be seen. In this class belong fuchsine, methyl

[1] *Ber. d. chem. Gesell.*, **32**, 1595 (1899).

[2] Freundlich: *Kapillarchemie*, p. 564 (1909).

violet, Nile blue, neutral red, etc. Krafft[1] has shown that many dyes which when dissolved in water are either true colloids or show some colloidal properties, become true solutions when dissolved in alcohol.

That colloids play a prominent part in dyeing is shown by the fact that *mordants* are frequently used to render the color more permanent. These mordants, such as aluminium chloride, acetate, etc., are either colloids, or are hydrolyzed by the water present and form colloids. These colloids react with the dyes. They may do so by having an electrical charge opposite to that of the dye, and both mordant and colloid dye being precipitated in the fibers of the fabrics to be dyed. This brings us to the various suggestions that have been made to account for the phenomena of dyeing.

Before the significance of colloids was known, dyeing was explained on purely chemical grounds. The salt of the dye was decomposed, the colored ion adhering to the fiber. Since dyeing often takes place under conditions where chemical reactions are excluded, this view is not sufficient.

After solutions in solids as solvents became clearly recognized as a type of true solutions (see next chapter), the bearing of them on dyeing was seen. Witt[2] suggested that in dyeing solid solutions are formed, the dye playing a rôle somewhat similar to the ether in the well-known Küster[3] experiment with solid solutions. The dye divides itself between the liquid that is present and the solid material to be dyed.

Some evidence in favor of the solid solution theory of dyeing has been furnished by the microscopic examination of the dyed materials. The dye does not seem to be limited to the surface of the fibers, but is distributed through the fiber. This would suggest solution of the dye-stuff in the solid fibers.

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[1] *Ber. d. chem. Gesell.*, **32**, 1608 (1899).

[2] *Färberzeit*, **15**, 1 (1890).

[3] *Zeit. phys. Chem.*, **13**, 445 (1894); **17**, 357 (1895).

After adsorption began to be studied quantitatively and analyzed mathematically, it was found that dyeing often obeyed the laws of adsorption. The substances to be dyed often took up the dye-stuff in quantities which, under given conditions, were essentially the same as when the dye was taken up by ordinary adsorbents. In a word, the adsorption equations held for the taking up of many dye-stuffs by many substances which were dyed by them. Schmidt[1] and Freundlich and Losev[2] showed that the amounts of the dye taken up from baths containing the dye at different concentrations could be calculated from the equations deduced from adsorption phenomena.

Enough is known about the phenomena of dyeing to force us to conclude that they are complex. There seems to be no question but that colloids play a prominent rôle. Solid solutions under certain conditions may be formed. All things considered, adsorption seems to be one of the most important phenomena.

When we have a comprehensive theory of dyeing, it will include what is true in all of these suggestions, as each of them probably contains an element of truth.

Other Technical Applications of Colloids. — Caoutchouc is a colloid, and in obtaining it from the plant juice other colloids come into play. The vulcanization of caoutchouc is dependent upon adsorption processes.

In the preparation of porcelain, colloids come prominently into play. Clay contains gels, and in the presence of water the properties of these substances manifest themselves, and to their presence is due to a large extent the plasticity of clay. Colloids come prominently to the front in the coloring of glass. We can now obtain glass of almost any color. We have glass which is red, the color being due to the presence of very fine colloidal particles of gold. Other red glass owes its color to small particles of copper. Other colors are due to cobalt or uranium compounds.

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[1] *Zeit. phys. Chem.*, **15**, 56 (1894).

[2] *Ibid.*, **59**, 284 (1907).

There are still a large number of applications of colloids to the industries which might be mentioned. Colloids play a rôle in the setting of cement, in the brewing of beer, but it would lead us beyond the scope and purpose of this chapter to consider in detail any of these matters.

ADSORPTION

It has long been known that charcoal has the power to take up certain gases like carbon dioxide in large quantities. It can also adsorb certain constituents from solutions. This fact has been utilized to the greatest advantage in such processes as the purification of sugar. The coloring matter from the solutions of sugar is removed by the charcoal, and a colorless product results.

Charcoal is not alone in possessing this adsorbing property. Many other substances in a fine state of division, *i.e.*, exposing large surfaces, have this same property. It is largely upon adsorption that dyeing depends. The soil particles adsorb plant food, and retain it at their surfaces. The term adsorb seems to have been introduced into the literature by du Bois Reymond. It implies that the substance taken up is held at the surface of the adsorbent, and is not in a state of chemical combination with it. On account of its importance from both a scientific and a technical standpoint, much work has been done recently on the nature of adsorption; how it is affected by changing the nature and quantity of the adsorbent; how by changes in the nature and quantity of the substance to be adsorbed; the effect of temperature on adsorption, etc.

This is the method which we follow in the case of true solutions. What is the effect on solubility of changing the nature of the solvent? What the effect of changing the nature of the substance to be dissolved? How is solubility affected by temperature, etc.

Nature of the Adsorbent. — Take first the *nature of the adsorbent.* How does this affect the adsorption? It is well known that solubility in true solution depends as much on the nature of the solvent, as of the dissolved substance; and from the solubility of one substance in a given solvent, we can draw no certain conclusion as to the solubility of another substance in that same solvent.

The adsorbing power of solids presents simpler relations. If a solid adsorbent adsorbs one substance more than it does another, then a second solid adsorbent will adsorb the first substance more than it will the second, and so on; showing a relation here which fails to manifest itself in the case of true solutions.

In dealing with the effect of the *nature of the substance adsorbed* when adsorption takes place in solution, we must take into account two variables — the *solvent* and the *dissolved substance.*

From aqueous solutions charcoal adsorbs acids, bases and salts only slightly; while organic substances, especially the aromatic compounds, are strongly adsorbed. From solutions in organic solvents the dissolved substances are only slightly adsorbed. The following data will illustrate this relation; the concentration of the benzoic acid in the several solvents is kept constant and is equal to 0.01 mol. per liter.

	Amount adsorbed in millimols
Benzoic acid in water	3.27
" " " benzene	0.54
" " " acetone	0.30
" " " ether	0.30

A general relation has been worked out between the adsorption of substances dissolved in any given solvent and the adsorption of that solvent when dissolved in other solvents. Solvents from which the dissolved substances are easily adsorbed, are, when dissolved in other solvents, only slightly adsorbed. The converse also holds: substances which from solutions are strongly adsorbed, when used as solvents yield solutions from which the dissolved substances are only slightly adsorbed. Thus, sulphuric acid, is, as we have seen, only slightly adsorbed from aqueous solutions. Therefore, substances dissolved in this solvent should show strong adsorption, and such is the case.

The phenomenon of adsorption is a *very rapid one.* The equilibrium between the substance to be adsorbed and the adsorbent is quickly reached. The following data for succinic acid adsorbed by carbon will confirm this conclusion, the amounts of acid adsorbed being expressed in milliequivalents per gram carbon.

Minutes	Amount adsorbed
5	0.183
10	0.325
30	0.752
60	1.06
∞	1.16

Effect of Temperature on Adsorption. — The effect of temperature on the ordinary processes of true solution is very pronounced. The temperature coefficients of solubility are usually large. Most substances dissolve far more at higher than at lower temperatures. For some compounds, however, exactly the reverse is true. Whether the temperature coefficient of solubility is positive or negative, it is usually of very considerable magnitude.

The influence of temperature on the adsorption of acetic acid from an aqueous solution by charcoal can be seen from the following data.

Temperatures	Adsorption
0°	1.15
50.2°	0.728
93.8°	0.466

While there may be no direct connection between adsorption phenomena and chemical reactions, there is certainly an indirect relation. Many gases are adsorbed in large quantities by certain solids. These gases are then present at the surfaces of the solids at high concentrations. They may be in a different physical, or even chemical state, than the free gases themselves. If oxygen is adsorbed by a solid, in this condition it will often effect oxidations which oxygen gas will not effect. The same is true of the activity of adsorbed hydrogen. It may have greater reducing power than hydrogen gas. These examples are sufficient to show that while adsorption as such is probably not a chemical phenomenon, it has an important chemical bearing, and is therefore of interest and importance to the chemist. One application of adsorption must be referred to. It has been shown by Dewar[1] and more recently by Pfund,[2] that the power of certain solids to adsorb gases can be used very effectively in producing high vacua. This is based upon the fact that gases are adsorbed more readily, in proportion to the amount of gas present, when dilute or at low pressures, than when more concentrated or under higher pressure.

Theories of Adsorption. — When gases and liquids are adsorbed by solids they disappear as such and are condensed on the surfaces of the solids. This condensation, especially in the case of a gas, would seem to lead to high pressures, and it has been assumed that at least adsorbed gases are under high pressures in or on the solid adsorbents. This same view of condensation has been extended from gases to liquids.

It has been pointed out that while the vapor-tension of a compressed liquid is higher than that of the same liquid under normal pressure, temperature remaining constant, the vapor-tension of an adsorbed liquid is less than that of the same liquid in the free state. Since at present we know so little of the real nature of adsorption, and of the real condition of and in adsorbed liquids, it is impossible to judge of the value of this objection.

The above conception of the condition of adsorbed substances has led to the view that adsorption is fundamentally connected with surface-tension. A study of the phenomena connected with surface-tension and those of adsorption has shown, however, that the two often seem to run counter to one another.

Other suggestions have been made to account for the

[1] *Proceed. Roy. Soc.*, **74**, 126 (1904).

[2] *Phys. Zeit.*, **13**, 870 (1912).

phenomena of adsorption. Lagergren,[1] from the Van't Hoff-le Chatelier principle, deduced the relation between the effect of pressure on solubility and the adsorption of the substance, on the assumption that adsorption is a condensation of the substance adsorbed on the surface of the adsorbent. Those substances which with increase in pressure are more soluble would be the more adsorbed. This pressure theory of adsorption is not entirely satisfactory.

Van Bemmelen,[2] Vaubel[3] and others have proposed a chemical theory of adsorption. They regard adsorption as a loose chemical combination between the adsorbent and the substance adsorbed. If there is any kind of chemical combination between the adsorbent and the substance adsorbed, it differs fundamentally from ordinary chemical combination. Adsorption does not obey the laws of definite proportions, and there are other serious objections to this view.

It has been suggested that in adsorption there is formed a solid solution between the adsorbent and the substance adsorbed. Such a solid solution may, to some extent, be formed after the adsorption has taken place; but this does not account for adsorption itself.

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[1] *Bihg. K. Svensk. Ak. Hand.*, **24,** 2, Nos. 4 and 5 (1899).

[2] *Journ. prakt. Chem.*, **23,** 324, 379 (1881); *Zeit. anorg. Chem.*, **23,** 111 (1900).

[3] *Ibid.*, **74,** 232 (1906).

CHAPTER XIII

SOLUTIONS IN SOLIDS AS SOLVENTS

We have thus far studied, first, solutions in gases as the solvents — gases, liquids and solids being the dissolved substances. We next took up in some detail and with some thoroughness solutions in liquids as the solvents — solutions of gases in liquids, of liquids in liquids and of solids in liquids. These were all true solutions. Then we studied colloidal solutions and colloidal suspensions in liquids as the solvents; and now it remains to study solutions in solids as the solvents.

With reference to solutions of gases and liquids in solids we know very little. Solids like charcoal dissolve gases, and the amount of the gas dissolved is increased by increasing the pressure to which it is subjected. Liquids are taken up by solids, sometimes in very considerable quantity and the liquid is often held with great tenacity. Glass which has been heated to redness in a vacuum for a month, will still give off water. In reference to solutions of gases and liquids in solids, other than a few superficial observations concerning them, we can say that our ignorance, even at present, is very nearly complete.

Solutions of Solids Dissolved in Solids, or Solid Solutions Proper. — When we come to solid solutions proper, or solutions of solids dissolved in solids, we can say we really know something, and our knowledge is of an interesting kind. The whole subject of solid solutions was opened up in a paper by Van't Hoff,[1] which appeared in 1890, bearing the title "Solid Solutions."

That mixtures of solids exist which have all the superficial appearances of being true solutions, is well known.

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[1] *Zeit. phys. Chem.*, **5**, 322 (1890).

Says Van't Hoff[1] "If we regard a solid solution as a solid, homogeneous mixture of several substances, the composition of which can be changed without destroying the homogeneity, analogous to solutions in liquids as the solvent, it would not be difficult to cite cases which belong unconditionally in this category."

"It would be expected that the number of cases of solids dissolving one another would be smaller than of liquids; just as the number of cases of liquids dissolving one another to an unlimited extent is smaller than of gases; yet we have many cases of two solids each dissolving the other."

"We may mention first 'isomorphous mixtures,' which best illustrate the point in question. The alums are good examples. They, like liquids, are miscible with one another in all proportions. There are also cases known which are comparable with the conditions illustrated by water and ether (limited miscibility); beryllium sulphate and selenate being examples."

Van't Hoff then takes up the discussion of "mixed crystals," as illustrating solid solutions; and concludes this part of the discussion with the following paragraph.

"In this connection we must not omit an interesting experiment carried out by Spring,[2] which shows indirectly with considerable certainty the reciprocal solubility of solids. When an equimolecular admixture of barium sulphate and sodium carbonate are subjected to pressure, he observed a double decomposition amounting to 20 per cent, which, on standing, increased to 80 per cent." This can be explained only on the assumption of partial miscibility of these solids.

Osmotic Pressure in Mixtures of Solids. — That solids can mix with solids, forming apparently homogeneous mixtures, is obvious from what has been said. The question is, are these homogeneous solids true solutions, or not?

This can be answered only by applying to them the tests of true solutions. What are the properties of true solutions? They must have osmotic pressure. The solute must lower the freezing-point of the solvent, and, if the boiling-point of the solute is considerably below that of the solvent, must lower its vapor-tension. Do these homogeneous mixtures of solids show all or any of these properties? These questions are answered by Van't Hoff in the paper referred to above.

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[1] *Zeit. phys. Chem.*, **5**, 323 (1890).

[2] *Bull. Soc. Chim.*, **44**, 166 (1885).

Take first the question of the existence of osmotic pressure in solid solutions. How can this be tested? Obviously not by any direct method of measurement, or even of demonstration. But while we cannot demonstrate directly the existence of osmotic pressure in mixtures of solids, we can prove it indirectly.

Osmotic pressure, as we have seen, is the cause of all diffusion. If we could prove the existence of diffusion in mixtures of solids, we would prove the existence of osmotic pressure in such mixtures. This is just what Van't Hoff has done.

He says,[1] "We need not be surprised that, whereas diffusion in gases takes place very rapidly and in liquids slowly, in solids it is so greatly retarded that the phenomenon long escaped observation. Yet it is now perfectly clear." Van't Hoff then refers to examples of diffusion in mixtures of solids. Spring had shown that when barium sulphate and sodium carbonate are pressed together and the pressure removed, the double decomposition proceeded after the removal of the pressure, until, after seven days, 80 percent of the sulphate had been transformed into carbonate. Diffusion must have taken place in this mixture of solids after the pressure was removed, bringing them into more intimate contact; and consequently the reaction proceeded until about three-fourths of the sulphate was transformed into carbonate. Bars of iron heated in carbon take up as much as five percent of the carbon. Colson[2] showed that the iron also

[1] *Zeit. phys. Chem.*, **5**, 325 (1890).

[2] *Compt. rend.*, **93**, 1074 (1881).

penetrated the carbon for a considerable distance even at 250°. Calcium was also shown to diffuse into iron, rendering it brittle.

Violle[1] heated porcelain crucibles in graphite and noted that the carbon penetrated the porcelain; and Marsden[2] showed that the carbon had gone through the porcelain.

Diffusion of solid through solid is also of practical importance. Gore has shown that zinc objects electroplated with a thin layer of copper, acquire on standing the zinc color, due to the diffusion of the zinc through the copper at ordinary temperatures.

Further, it was pointed out by Colson that platinum surrounded on all sides by carbon which was free from silicon, when heated in a porcelain crucible took up silicon from the crucible although the platinum did not come in contact with the crucible at any point. This showed that the silicon from the crucible had passed through the carbon into the platinum.

One of the best examples of the diffusion of metals into metals is that brought out by Roberts-Austen,[3] working at the mint of England. He took cylinders of lead and polished their ends. He then took discs of gold and polished their faces. He tied the gold discs on to the lead plates and placed these solids in the vault at ordinary temperatures. The two metals were allowed to stand in contact for about four years, when it was found that the discs had stuck to the lead. These gold discs were removed and sections of the lead cylinders cut and analyzed. The gold was found to have penetrated into the lead nearly a centimeter, the lead sections nearest the gold plate being richest in gold. Here is an example of a resistant metal like gold, diffusing into a metal like lead at ordinary temperatures, in quantities which can be easily measured.

Van't Hoff[4] then attempts to demonstrate *directly* the existence of osmotic pressure in mixtures of solids, but

[1] *Compt. rend.*, **94**, 28 (1882).

[2] *Proc. Edinb. Soc.*, **10**, 712.

[3] *Proceed. Roy. Soc.*, **67**, 101 (1900).

[4] *Zeit. phys. Chem.*, **5**, 327 (1890).

since his method of proof does not seem to be free from objection, it will not be discussed here.

Lowering of the Vapor-Tension of Solids by Other Solids. — We have seen that a second fundamental and characteristic property of true solutions is the power of the dissolved substance to lower the vapor-tension of the solvent, provided the solute boils considerably higher than the solvent. The question here is, have we in mixtures of solids any evidence that the one solid lowers the vapor-tension of the other?

Van't Hoff points out that Hauer[1] had shown that such is the case. Lead dithionate is a salt which readily decrepitates. This means a solid salt of which the water has a relatively high vapor-tension at ordinary temperatures — so high that it blows the salt to pieces when it is heated. When an isomorphous crystal of lead and calcium or strontium dithionate was obtained, this was found to decrepitate much less than the pure lead salt; showing that the presence of the calcium or strontium salt had lowered the vapor-tension of the lead salt.

We cannot hope to test the above question in any general way, on account of the very small vapor-tensions of solids, and the small percentage lowering of this very small quantity by the presence of one solid dissolved in another solid. Wherever we can test the question, however, we find that in the mixed solids one has lowered the vapor-tension of the other.

Another example illustrating the same point that was referred to above, is the lowering of the vapor-tension of iron alum by forming with it an isomorphous mixture of aluminium alum. Similarly, the vapor-tension of copper formate is lowered by the presence in the solid crystal of barium or strontium formate. Van't Hoff adds,[2] "Let it be clearly understood that we are not dealing here with a lowering of vapor-tension caused by admixture with substances of smaller vapor-tension; the mixtures show, by their decrepitation, a smaller tension than either of the constituents."

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[1] *Verhandl. Kaiserl. Königl. geol. Reichsan.*, 163 (1877).

[2] *Zeit. phys. Chem.*, 5, 330 (1890).

Lowering of the Freezing-Point of a Solid by Another Solid. — This brings us to the third necessary and sufficient property to have a true solution — the lowering of the freezing-point of the solvent by the dissolved substance. Have we any evidence that one solid lowers the freezing-point of another solid with which it is mixed? There is an abundance of evidence.

The alloys illustrate this. Two are especially well known — Rose's and Wood's fusible metals. The former contains one part lead, one part tin and two parts bismuth; the latter contains two parts lead, one part tin, four parts of bismuth and one part of cadmium.

Lead melts at	327°	Rose's metal melts at	94°
Tin melts at	232°	Wood's metal melts at	71°
Bismuth melts at	268°		
Cadmium melts at	321°		

An alloy[1] containing 15 bismuth, 8 lead, 4 tin, and 3 cadmium melts at 60°.

We do not need any better illustration than this of one solid lowering the freezing-point of another solid with which it is mixed.

We have thus shown that the three fundamental properties which characterize solutions in liquids as solvents, are present to some extent in mixtures of solids with one another, and we are therefore justified in regarding such mixtures of solids as true solutions.

Van't Hoff, in the paper already referred to, worked out a method for determining the molecular weights of solids in solid solutions; but it would lead us too far to discuss his method in detail here, especially since it cannot be regarded as having led to results of any great significance.

The same may be said of the method worked out by Küster[2] for determining the molecular weights of substances in solid solutions. In the opinion of the author, a perfectly frank statement of the situation with respect to solid solutions, and the molecular weights of solids in such solutions, would be about as follows. We do not know with even a reasonable degree of probability the molecular weight of even the simplest substance in the solid state; and we do not know the molecular weight of any solid in a solid solution with any certainty.

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[1] Erdmann: *Lehrb. d. anorgan. Chemie*, p. 684 (1906).

[2] *Zeit. phys. Chem.*, **13**, 445 (1894); **17**, 357 (1895).

Thus we see that, while our ignorance of solid solutions cannot at present be said to be quite perfect, still it is not widely removed from it. Our knowledge both of pure solids and of solid solutions is very meager. We have just scratched the surface, so to speak, of matter in the solid state.

CHAPTER XIV

THE NEWER HYDRATE THEORY

About sixteen years ago the work which led to the present hydrate theory of aqueous solution was begun in this laboratory. From a very simple beginning, which did not have for its object the study of the nature of solution in general, the work has widened in a number of directions. Much of this work has been carried out with the aid of grants generously awarded by the Carnegie Institution of Washington; this and the following chapter are taken with the permission of the Institution largely from Publication of the Carnegie Institution of Washington No. 210, Chapter VII.

Earlier Work. — In 1899 the author's co-operators Ota[1] and Knight[2] brought to light certain facts which could not be explained in terms of any relation that was then known. They found that certain double salts, such as double chlorides, nitrates, sulphates, cyanides, etc., produced abnormally great lowering of the freezing-point of water when the solutions were concentrated. What was more perplexing was the fact that the *molecular depression of the freezing-point increased with the concentration* beyond a certain definite concentration.

Similar results were found for a fairly large number of salts by Jones and Chambers,[3] and by Chambers and Frazer working with Jones.[4] The salts studied by these workers were those that are known to be very hygroscopic, to have great power of combining with water. The question arose, what did these results mean? At that time, the writer was antagonistic to any hydrate theory, regarding the ions in solution as having an existence not only independent of one another, but also independent of the molecules of the solvent. This seemed to be the view which was held at that time also by most of those who founded the new school of chemistry.

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[1] *Amer. Chem., Journ.*, **22**, 5 (1899).

[2] *Ibid.*, **22**, 110 (1899).

[3] *Ibid.*, **23**, 89 (1900).

[4] *Ibid.*, **23**, 512 (1900).

Yet it seemed impossible to interpret the results obtained in terms of any other assumption than that a part of the water present was combined with the dissolved substance, and was therefore removed from playing the rôle of solvent. Accordingly, in 1900,[1] the suggestion was ventured, for want of any better, that hydration in aqueous solution would explain these results. If a part of the water present is combined with the dissolved substance, there would be less water acting as solvent; and since freezing-point lowering is proportional to the ratio between the number of molecules of the solvent and of the dissolved substance, the less solvent present the greater the lowering of its freezing-point. It is one thing to make a suggestion which accounts for the known facts; it is a very different matter to show that this is the only reasonable suggestion which will account for them, to show that the suggestion is true.

Aided by a grant from the Carnegie Institution of Washington, the author started Dr. Getman[2] on a more or less systematic study of the whole problem. The question arose, were the results already obtained limited to a few compounds, or types of compounds, or was this a general phenomenon? To answer this the study of acids, bases, and salts in concentrated solutions, especially by the freezing-point and conductivity methods was taken up and the refractivities of many solutions determined.

Relation Between Lowering of the Freezing-Point of Water and Water of Crystallization of the Dissolved Substance. — The work of Getman included the study of the lowering of the freezing-point of water produced by concentrated solutions of the chlorides, bromides, iodides and nitrates of a large number of metals. The relation between lowering of freezing-point and water of crystallization can be seen very well from the curves for the chlorides and nitrates.[1]

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[1] *Amer. Chem. Journ.*, **23**, 103 (1900).

[2] *Ibid.*, **27**, 433 (1902); **31**, 303 (1904); **32**, 308 (1904); *Zeit. phys. Chem.*, **46**, 244 (1903); **49**, 385 (1904); *Phys. Rev.*, **18**, 146 (1904); *Ber. d. chem. Gesell.*, **37**, 1511 (1904).

The nitrates of sodium, potassium, and ammonium, which crystallize without water, produce the smallest lowering of the freezing-point of water. Then come the nitrate of lithium with 2 molecules of water, calcium with 4, and a large number of nitrates each with 6 molecules of crystal water; all give about the same lowering of the freezing-point. Finally, the three nitrates of aluminium, iron, and chromium with 8 and 9 molecules of water, give the greatest lowering of the freezing-point of water.

Relations similar to the above come out for the chlorides, the bromides and the iodides.[2] The freezing-point lowerings of water produced by them are roughly proportional to the amounts of water with which the salts crystallize.

If, on the other hand, we compare the chlorides with the bromides, with the iodides, with the nitrates, similar relations manifest themselves.

It was found that chlorides, bromides, iodides and nitrates which have no water of crystallization, all produce about the same molecular lowering of the freezing-point of water, and this is between 3° and 4°. With salts that crystallize without water there is only a very slight increase in the molecular lowering of the freezing-point with increase in the concentration of the solution. The salts of lithium, which crystallize with the same amounts of water, give approximately the same depressions of the freezing-point.

If we compare the salts of the alkaline earths that crystallize with 6 molecules of water, we find that they produce approximately the same lowerings; the nitrates of iron and aluminium with 8 and 9 molecules of water give greater lowerings than the corresponding halogen salts with 6.

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[1] See *Carnegie Institution of Washington*, Publication No. 60, p. 24 (1907).

[2] *Ibid.*, pp. 20–26 (1907).

In the first case we have kept the acid constant and compared with one another the salts of the different metals with the same acid. In the second case we have kept the metal constant, and compared the salts of a given metal with different acids. In both cases the relation between lowering of the freezing-point of water by the dissolved substance and water of crystallization of the dissolved substance manifests itself.

Those salts that crystallize with the largest amounts of water produce the greatest molecular lowering of the freezing-point of water. The work was done with concentrated solutions, and it has already been pointed out that for such substances the molecular lowering of the freezing-point increases with the concentration of the solution.

We must now ask, what bearing has this relation on the question of hydration or non-hydration in aqueous solution? A moment's thought will show that the bearing is a very direct one. If hydrates exist in aqueous solution, those substances which in such solutions would form the most complex hydrates would be the substances that would crystallize from aqueous solutions with the largest amounts of water. This is the same as to say that those substances which, in the presence of a large amount of water, have the greatest power to combine with water, would, other things being equal, be the ones to bring with them out of aqueous solution the largest amounts of water as water of crystallization.

We could not, however, expect one of these phenomena to be strictly a linear function of the other, since there are undoubtedly other factors, such as shape of molecules, angles of crystals, etc., coming into play in determining the exact composition of crystals.

That a relation such as was pointed out above holds so well and so generally for such a large number of substances is very significant, and pointed to the fact that the suggestion of hydration in general in aqueous solution contained more truth than was imagined when it was first suggested.

Having found a relation such as the above, it seemed desirable to look about for others that would bear directly or indirectly on the problem in hand. Before taking up these, another feature of the work of Getman must be briefly discussed.

Approximate Composition of the Hydrates Formed by Various Substances in Solution. — The line of evidence just discussed seemed so strongly in favor of the general correctness of the view that there is combination between the dissolved substance and some of the water present, that Jones and Getman[1] undertook to calculate the approximate composition of the hydrates formed by the different substances, and by the same substance at different dilutions.

The experimental work consisted in determining the freezing-point of the solution and, consequently, the depression of the freezing-point of water produced by the dissolved substance at the concentration in question. From the freezing-point lowering the molecular lowering was calculated.

The dissociation of the solution was measured by means of the conductivity method. Knowing the dissociation, the theoretical molecular lowering was calculated on the assumption that none of the solvent was combined with the dissolved substance. The ratio of the theoretical molecular lowering to the value found experimentally gave the proportion of all the water present that was uncombined. The remainder of the water was, of course, combined with the dissolved substance. The total amount of water present in any given solution could be readily determined. It was only necessary to take the specific gravity of the solution by weighing a known volume of it. Knowing the specific gravity and the concentration, it was, of course, quite simple to determine the total amount of water in, say, a liter of the solution. The total amount of water in the solution and the percentage of combined water being known, the total amount of combined water was known. Knowing the amount of dissolved substance present in a liter of the solution, and knowing the total amount of water combined with it, it was a simple matter to calculate from the molecular weights of the dissolved substance and the solvent how many molecules of water were combined with one molecule of the dissolved substance. The results of such a calculation are only approximations. In the first place, the conductivity method of measuring dissociation is not sufficiently accurate for concentrated solutions, and there is no thoroughly reliable method known for this purpose. The error here is, however, in all probability not very large. Another source of error, which is probably larger, results from the assumption that Raoult's law holds for concentrated solutions, *i.e.*, that for concentrated solutions the lowering of the freezing-point is proportional to the concentration. This is not strictly the case, and we do not know at present how wide the deviation from Raoult's law is in concentrated solutions.

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[1] *Carnegie Institution of Washington,* Publication No. 60 (1907).

Taking all of these factors into account, it still seems highly probable that, by the method outlined above, we can arrive at a reasonably close approximation to the amount of water combined with a molecule, or the resulting ions, of a dissolved substance, under given conditions of concentration. Whatever objection may be offered to this method of calculating the approximate composition of the hydrates existing in aqueous solution, it should be stated that, so far as the writer knows, it is the only general method thus far worked out for throwing any light whatever on this important problem. Jones and Getman applied this method of calculating the approximate composition of hydrates to about 100 compounds — salts, acids, and organic substances — and to about 1,500 solutions of these substances. Their results have been recorded in Publication No. 60 of the Carnegie Institution of Washington.

A few results for strongly hydrated salts will show the order of magnitude of the hydration for such substances. In the first column is given the concentration in terms of gram-molecular normal. In the second, the number of molecules of water combined with one molecule of the dissolved substance at the concentration in question.

Magnesium chloride		Chromium chloride	
0.15	52.1	0.1	66.6
0.20	49.7	0.2	49.6
0.25	43.3	0.3	42.5
0.38	33.2	0.4	39.2
0.50	29.4	0.5	39.2
0.61	28.3	0.6	35.3
0.93	25.8	0.7	35.8
1.4	21.4	0.9	31.8
1.8	19.0	1.0	30.9
2.3	17.4	1.5	26.0
		2.0	22.1

Salts of lithium form more complex hydrates than those of sodium and potassium. This would be expected, since lithium salts crystallize with water, while the salts of the other alkalies in general crystallize without water.

Salts of potassium and ammonium generally crystallize without water, and these compounds, as would be expected, combine with relatively little water in aqueous solution.

Many salts of sodium crystallize without water, and these hydrate very slightly. Other sodium salts, such as the bromide and iodide, crystallize with water and show considerable hydrating power in solution.

Salts of calcium crystallize with water and all have, as would be expected, large hydrating power. The halogen salts crystallize with 6, the nitrate with 4 molecules of water. The nitrate was found to have less hydrating power than the chloride or bromide.

The salts of strontium resemble those of calcium, both in the amounts of water with which they crystallize and with which they combine in aqueous solution. Salts of barium crystallize with less water and show less hydration than those of calcium and strontium.

The salts of magnesium have just about the hydration that would be expected from their water of crystallization. The same may be said of the salt of zinc that was studied.

Cadmium is of special interest. Its halogen compounds crystallize with little or no water, and although cadmium belongs in the same group with metals of large hydrating power, its halogen salts combine with only a small amount of water. The nitrate of cadmium crystallizes with 4 molecules of water and, as could be predicted, shows considerable hydrating power.

The chloride and nitrate of magnesium show the hydration that would be expected from their water of crystallization. The same may be said of the salts of nickel, cobalt, and copper.

The chlorides and nitrates of aluminium, iron, and chromium crystallize with large amounts of water and show great hydrating power.

The strong mineral acids show some hydrating power, but the complexity of the hydrate formed by these substances seems to pass through a maximum. The acids thus differ from the salts.

Some 13 non-electrolytes were studied as to their hydration, and none of them showed any appreciable hydration. The same applies to the organic acids that were studied in this connection.

The following general relations were brought out by the work of Jones and Getman. The total amount of water held in combination by the dissolved substance increases as the concentration of the solution increases. From what is known of mass action, this would be expected.

The number of molecules of water combined with one molecule of the dissolved substance generally increases from the most concentrated to the most dilute solution studied. In some cases, however, the number of molecules of combined water seems to pass through a maximum. These results, it is believed, give us approximately the amounts of combined water and certainly the relative hydrating powers of the different compounds studied.

Relation Between Water of Crystallization and Temperature of Crystallization. — Jones and Bassett[1] worked out the approximate composition of the hydrates formed by a large number of substances and also the following relation. The hydrates, as we have seen, are very unstable systems. They are readily broken down in solution with rise in temperature. The hydrates which exist in solution at ordinary temperatures are much more complex than those which the salts can bring with them out of solution as water of crystallization. The hydrates are more stable and more complex the lower the temperatures. We were, however, surprised, on examining the literature, to find the large number of examples on record of salts crystallizing with varying amounts of water, depending on the temperature at which the crystals were formed.

A few examples will be given to bring out the general relation that the number of molecules of water of crystallization is larger the lower the temperature at which the salt crystallizes.

$CaCl_2$	H_2O	As the temperature of crystallization is lower and lower.
	$2\ H_2O$	
	$4\ H_2O$	
	$6\ H_2O$	
$MnCl_2$	$2\ H_2O$....	20°
	$4\ H_2O$....	15°
	$6\ H_2O$....	– 21°
	$11\ H_2O$....	– 21° to – 37°
	$12\ H_2O$....	– 48°
$FeCl_3$	anhydrous..	80° and above
	$2\ H_2O$....	60° to 80°
	$2\frac{1}{2}\ H_2O$....	40° to 60°

$MgCl_2$	$6\ H_2O$	Elevated temperatures above 20
	$8\ H_2O$	
	$10\ H_2O$..	20°
	$12\ H_2O$..	– 10° to – 12°
$MnSO_4$	$3\ H_2O$..	25° to 31°
	$4\ H_2O$...	25° to 31°
	$5\ H_2O$...	15° to 20°
	$7\ H_2O$...	0° or below 0°
$FeCl_3$	$3\frac{1}{2}\ H_2O$...	20°
	$6\ H_2O$...	20° to – 16°

These examples suffice to show the general nature of the relation between water of crystallization and the temperature at which the salt crystallizes. This relation could have been foreseen as a necessary consequence of the theory of hydrates in aqueous solution, and the instability of those hydrates at higher temperatures.

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[1] *Carnegie Institution of Washington*, Publication No. 60 (1907). *Amer. Chem. Journ.*, **33**, 534 (1905); **34**, 291 (1905). *Zeit. phys. Chem.*, **52**, 231 (1905).

Dissociation as Measured by the Freezing-Point Method and by the Conductivity Method. — When the theory of electrolytic dissociation was proposed, it became a problem to measure accurately the magnitude of dissociation. Arrhenius pointed out, in his original epoch-making paper, that dissociation could be measured either by the freezing-point or by the conductivity method.

Ostwald so improved the freezing-point method that it could be used to measure dissociation.

A comparison of the data from the freezing-point method with those from the conductivity method showed that dissociation as measured by the former was slightly higher than by the latter. (See p. 131). The meaning of this discrepancy was at that time not understood.

After it had been established, with reasonable certainty, that hydration takes place in aqueous solution, a possible explanation of this apparent discrepancy presented itself. But before offering this explanation it seemed desirable to do more experimental work, having this point especially in mind. Pearce[1] carried out in this laboratory a very careful piece of work, in which dissociation was measured by the freezing-point method and also by the conductivity method, and the two sets of results were compared. The chlorides of calcium, strontium, magnesium, barium, cobalt, copper, and aluminium and the nitrates of calcium, magnesium, barium, cobalt, nickel and copper were studied as well as sodium bromide and hydrochloric, nitric and sulphuric acids.

That hydration can explain the fact that dissociation as measured by freezing-point is higher than as measured by conductivity can be seen from the following. The combined water is removed from the field of action as solvent; only the uncombined water is acting as solvent. Freezing-point lowering is proportional to the ratio between the number of molecules of the dissolved substance and of the solvent. If one-fourth of the water present is combined with the dissolved substance, the freezing-point lowering would be one-third greater than if all the water were present as free water and therefore acting as solvent water. Freezing-point lowering would thus be affected proportionally by hydration. Dissociation of concentrated solutions calculated from the freezing-point lowering would therefore be much too high.

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[1] *Carnegie Institution of Washington,* Publication No. 180, p. 57.

The conductivity of a solution depends upon the number of ions present and their velocities. The number of ions would probably not be affected greatly by the hydration, but their velocities would be. The hydrated ions would, of course, move more slowly than the unhydrated.

The effect of hydration would obviously be more pronounced on freezing-point lowering, which is proportional to the amount of solvent present, than on conductivity.

Temperature Coefficients of Conductivity and Hydration. — A fairly elaborate investigation on the conductivities, dissociation, and temperature coefficients of conductivity and dissociation of aqueous solutions was begun in the author's laboratory about 15 years ago. The work, as a whole, has been recently published by the Carnegie Institution of Washington.[1] The monograph in question contains the investigations of Clover,[2] Hosford,[3] Howard,[4] Jacobson,[5] Kreider,[6] Shaeffer,[7] Smith,[8] Springer,[9] West,[10] Wight,[11] Wightman,[12] and Winston.[13] The results published in this monograph are for about 110 salts, which were studied from zero to 65°, and from the most concentrated solution that could be used to the dilution, in most cases, of complete dissociation. The temperature coefficients of conductivity were calculated both in conductivity units and in percentage.

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[1] *Carnegie Institution of Washington*, Publication No. 170 (1912).

[2] *Amer. Chem. Journ.*, **43**, 187 (1910).

[3] *Ibid.*, **46**, 240 (1911).

[4] *Ibid.*, **48**, 500 (1912).

[5] *Ibid.*, **40**, 355 (1908).

[6] *Ibid.*, **45**, 282 (1911).

[7] *Ibid.*, **49**, 207 (1913).

[8] *Ibid.*, **50**, 1 (1913).

[9] *Ibid.*, **48**, 411 (1912).

[10] *Ibid.*, **44**, 508 (1910).

[11] *Ibid.*, **42**, 520 (1909); **44**, 159 (1910).

[12] *Ibid.*, **46**, 56 (1911); **48**, 320 (1912).

[13] *Ibid.*, **46**, 368 (1911).

Similar data were obtained for about 90 of the more common organic acids, and the constants for the weaker acids were calculated from the Ostwald dilution law. The dissociations of the salts and acids at the different temperatures were also calculated whenever possible.

The temperature coefficients of conductivity were calculated both in percentage and in conductivity units. A study of the temperature coefficients of conductivity, expressed in conductivity units, brought out a relation which had a very direct bearing on the question of hydration in aqueous solution. This is so important that it will be discussed here in some detail.

The conductivity of a solution is conditioned by the number of ions present and the velocities with which they move. Rise in temperature not only does not increase the number of ions present, but, as is well known, diminishes dissociation. The effect of rise in temperature increasing the conductivity of solutions is, then, due to an increase in the velocities with which the ions move. If the ion is driven by a constant force, its velocity would be determined chiefly by the viscosity of the solvent and by the mass and size of the ion. With rise in temperature the driving force would be increased. Rise in temperature would also decrease the viscosity of the solvent. The effect of rise in temperature on both of these factors would be to increase the velocities of the ions and, consequently, the conductivity.

Another factor must, however, be taken into account. That many ions in aqueous solutions are strongly hydrated seems now quite generally accepted. We have seen that these hydrates are relatively unstable and break down with rise in temperature. The simpler the hydrate formed by an ion, the smaller the mass of the ion; the smaller the mass of the ion, other things being equal, the less resistance it will offer when moving through the solvent. Therefore, rise in temperature should increase the velocity of the ion.

Coefficients for Slightly Hydrated Salts

Table A.— *Temperature coefficients of conductivity*

Substances with slight hydrating power	Temperature coefficients in conductivity units			
	25° to 35°		50° to 65°	
	$v = 8$	$v = 1024$	$v = 8$	$v = 1024$
Sodium chloride	2.00	2.46	2.27	2.82
Sodium bromide	1.89	....	2.18	2.79
Sodium iodide	2.12	2.54	2.33	3.14
Sodium nitrate	2.04	2.45	2.02	2.67
Potassium chloride	2.39	2.84	2.45	3.11
Potassium bromide	2.43	2.91	2.45	3.11
Potassium iodide	2.38	2.91	2.65	3.37
Potassium nitrate	2.08	2.16	2.31	2.83
Potassium permanganate	2.04	2.31	2.29	2.23
Potassium sulphocyanate	2.20	2.56	2.34	....
Ammonium chloride	2.42	2.94	2.51	3.69
Ammonium bromide	2.32	2.86	2.58	3.11
Ammonium nitrate	2.17	2.50	2.33	3.04

If decreasing complexity of the hydrate formed by the ion with rise in temperature plays any prominent part in determining the large temperature coefficients of conductivity, since the complexity of such hydrates would decrease more with rise in temperature, we should expect to find that *the ions which have the greatest hydrating power would have the largest temperature coefficients of conductivity.* This is a concrete and, it would seem, necessary consequence of the theory of hydrates in aqueous solutions. Further, it is one which can be tested directly by experiment. Is it true?

We have seen that the hydrating power of a salt, or the ions into which it dissociates, is approximately proportional to the number of molecules of water with which it crystallizes. This is the same as to say that the salt which has the greatest power to bring water with it out of solution is the one, other things being equal, which would hold the largest number of molecules of water in combination with it in solution. The question is, therefore, is there any relation between the number of molecules of water with which a salt crystallizes and its temperature coefficients of conductivity?

This relation has already been discussed in Publication No. 170 of the Carnegie Institution of Washington, in which the results of the work on conductivity and dissociation have been published. Tables A and B showing temperature coefficients in conductivity units between the temperatures 25° and 35°, on the one hand, and between 50° and 65° on the other, at the dilutions $\frac{1}{8}$ and $\frac{1}{1024}$ normal, are taken from the monograph referred to above.

COEFFICIENTS FOR STRONGLY HYDRATED SALTS

TABLE B.— *Temperature coefficients of conductivity*

Substances with large hydrating power	Temperature coefficients in conductivity units			
	25° to 35°		50° to 65°	
	$v = 8$	$v = 1024$	$v = 8$	$v = 1024$
Calcium chloride	3.49	4.85	....	....
Calcium bromide	3.73	5.00	4.03	6.03
Calcium nitrate	3.09	4.79	3.33	....
Strontium chloride	3.37	5.13	3.92	6.02
Strontium bromide	3.66	5.27	4.08	....
Strontium nitrate	2.76	4.86	3.58	....
Barium nitrate	3.09	4.74	3.34	....
Magnesium chloride	3.40	4.72	3.61	....
Magnesium bromide	3.55	4.44	4.08	....
Magnesium nitrate	3.10	4.78	3.57	....
Zinc nitrate	3.13	4.47	3.43	5.41
Nickel chloride	3.41	5.04	3.61	....
Nickel nitrate	3.21	4.58	....	....
Cobalt chloride	3.39	4.95	3.54	....
Cobalt bromide	3.32	4.96	3.75	....
Cobalt nitrate	3.20	4.67	3.05	....
Cupric nitrate	3.18	4.88	....	....
Aluminium chloride	4.57	8.64	5.16	12.49
Aluminium nitrate	4.19	7.86	4.87	11.65

We have seen that the hydrates formed by a large number of salts, including those given in tables A and B have already been worked out,[1] and that water of crystallization is a rough measure of water of hydration. The salts in table A crystallize with little or no water, and in aqueous solution are very little hydrated; those in table B in general crystallize with large amounts of water and are strongly hydrated compounds.

Let us compare the temperature coefficients of conductivity in conductivity units (which are the actual increases in molecular conductivity per degree rise in temperature) of the substances in table A with those in table B. It will be seen that the coefficients for the substances in table A are, at all dilutions and temperatures, much smaller than those in table B. In making this comparison we must, of course, take into account the fact that the substances in table A are binary electrolytes, each molecule breaking down into 2 ions, while the substances recorded in table B are all ternary electrolytes, each molecule breaking down into 3 ions, except the two salts of aluminium which are quaternary electrolytes, each molecule yielding 4 ions. Even taking all of these facts into account the temperature coefficients of conductivity for the slightly hydrated salts are much smaller than those for the strongly hydrated compounds. This is exactly what would be expected. The complexity of the hydrates of slightly hydrated salts could change only a little with rise in temperature. Consequently, the mass of the hydrated ion would change only slightly with rise in temperature, and this effect of temperature on conductivity would be very small.

Relations Between the Coefficients. — Another relation manifests itself when we compare the results in table A with one another, and those in table B with one another. If the temperature coefficient of conductivity is a function of the decreasing complexity of the hydrate formed by the ion, *as the temperature is raised we should expect that those substances which have equal hydrating power would have approximately the same temperature coefficients of conductivity.*

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[1] *Carnegie Institution of Washington,* Publication No. 60 (1907).

The substances in table A have only slight hydrating power, shown by the fact that they crystallize with little or no water. The fact is, their temperature coefficients of conductivity are all of the same order of magnitude.

The salts in table B have different hydrating powers, but all have large hydrating power. They have temperature coefficients of conductivity of the same order of magnitude, with the exception of the salts of aluminium.

The chloride of aluminium crystallizes with 6 molecules of water and the nitrate with 8. These salts, as has already been pointed out, break down yielding 4 ions each. Their temperature coefficients are larger than those of the ternary electrolytes.

The more dilute the solution, the more complex the hydrate formed by the molecule or the ion. This is but the expression of the action of mass; the more water there is present, the more will be combined with the dissolved substance. The more complex the hydrate the greater the change in the complexity of the hydrate with rise in temperature. Since the magnitude of the temperature coefficients of conductivity seems to be a function of the change in the complexity of the hydrate with rise in temperature, it follows, from the hydrate theory, *that the temperature coefficients of conductivity for any given substance should be greater at the higher dilution than at the lower.*

A comparison of the results at the two dilutions for any given substance in table A or table B will show that the above consequence of the hydrate theory is confirmed by the facts. The temperature coefficients are larger at the higher dilution for every substance recorded in both tables.

One other relation should be pointed out before leaving the discussion of the temperature coefficients of conductivity. We have seen that the hydrates are unstable, and that with rise in temperature they break down. The higher the temperature to which they are heated the more unstable they become. We should, therefore, expect the hydrates to break down more rapidly as the temperature goes higher. If this were the case, *the higher the temperature of the solution, the larger the temperature coefficients of conductivity.* If we compare the results for any given substance in table A or B we will find that such is the case. The temperature coefficients for any given dilution are higher between 50° and 65° than between 25° and 35°.

The above four conclusions from the solvate theory of solution, as far as aqueous solutions are concerned, are confirmed at every point by the results of measuring the temperature coefficients of conductivity. Without this theory it does not appear to be simple to explain the above relations. The agreement between the four deductions from the theory and the experimental results is so satisfactory that it is regarded as strong evidence in favor of the general correctness of the theory.

Relation Between the Hydration of the Ions and Their Ionic Volumes. — Jones and Pearce[1] worked out the approximate composition of the hydrates formed by a large number of salts, using the freezing-point and conductivity methods already referred to. They found the following relation between the volumes of the ions and their power to form hydrates. The atomic volume curve[2] is obtained by plotting the atomic weights of the elements as abscissae against the atomic volumes as ordinates. This curve, as is well known, contains well-defined maxima and minima. At the maxima are the alkali elements, the three with the largest atomic volumes being potassium, rubidium and caesium. The salts of these elements generally crystallize without water, and therefore have very little hydrating power in aqueous solution. The approximate hydration[1] of salts of potassium has been determined by the method usually employed and has been found to be small.

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[1] *Carnegie Institution of Washington*, Publication No. 180, p. 57 (1913); *Amer. Chem. Journ.*, **38**, 736 (1907).

[2] See *Elements of Physical Chemistry*, by the author, 4th edition, p. 29. (The Macmillan Co.)

Some of the salts of lithium and sodium crystallize with 2 and 3 molecules of water, and these have been shown to have some hydrating power.[1] The atomic volumes of lithium and sodium are much smaller than those of potassium, rubidium, and caesium.

Turning from the maxima of the curve to the minima, at the mininum of the third section of the curve are iron, cobalt, nickel, and copper. Salts of these metals crystallize with large amounts of water, and in aqueous solution they form complex hydrates.

Aluminium falls at the second minimum of the atomic volume curve, having a somewhat greater atomic volume than iron. The salts of aluminium crystallize with large amounts of water, some of them with 6 and 8 molecules. In aqueous solution they form complex hydrates.[2] Barium has the largest atomic volume of members of its group; its salts crystallize without water or some with 2 molecules of water. Many of the salts of calcium, strontium, and magnesium crystallize with 6 molecules of water. Magnesium has the smallest volume of any element of this group; it has been found to have the greatest hydrating power of any member of the group. Strontium has a slightly larger atomic volume than calcium and has a somewhat smaller power to form hydrates. Taking all of the facts into account, it would seem that, other things being equal, the *smaller the cation the greater its hydrating power*. This raises the question, which ion is it that forms the hydrate? Do both ions form hydrates? If so, which has the greater hydrating power?

The different salts of certain metals have approximately the same hydrating power. The common constituent of these salts is of course the cation, the anion varying from salt to salt. This would indicate that it is primarily the cation which conditions the hydrating power of a salt. Since the different salts of the same metal do not all have the same hydrating power, it seems reasonable to assume that the anion has some power to form hydrates in the presence of water. The cation is, then, the chief hydrating agent, and its hydrating power seems to be a function of its size or atomic volume — the smaller the ion the greater its power to hold water in combination with it in aqueous solution.

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[1] *Carnegie Institution of Washington*, Publication No. 60 (1907). [2] *Ibid.*

This raises the question, why is this the case? It has occurred to the writer that the electrical density of the charge on the ion may have something to do with this relation. Other things being equal, the smaller ion has the greater density of charge upon its surface; this might enable it to hold more molecules of water in combination with itself. There seem, however, to be certain physical objections to this explanation of the relation in question. Whatever the explanation, the fact remains.

Hydration of the Ions and the Velocities with Which they Move. — Certain apparent discrepancies presented themselves in the velocities of the different ions, which, for a time, could not be explained. It was known that the lithium ion, under the same driving force, moves more slowly than potassium; and yet it has smaller volume and smaller mass. It was not until it was shown[1] that the lithium ion is more strongly hydrated than sodium or potassium that this fact could be explained, and other apparent discrepancies presented themselves. A relation between the migration velocities of the ions and their hydrating power was worked out by Jones and Pearce.[2] Their discussion is repeated here to bring out the point in question.

The velocities of the ions in moving through any given medium may be assumed to vary inversely as their mass, the driving force being constant. Their velocities would also vary inversely as their volumes. Mass being constant, we should expect the ions with the smallest atomic volumes to move the swiftest under a constant driving force, while the facts are often the opposite. Leaving out of account the hydrogen and hydroxyl ions, potassium, rubidium, and caesium have very great velocities and the largest volumes; while the ions of the iron and copper group have the smallest volumes and very small velocities. The meaning of this apparent discrepancy can be seen at once by comparing the atomic volume curve and the migration velocity curve.

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[1] *Carnegie Institution of Washington,* Publication No. 60 (1907).

[2] *Ibid.*, Publication No. 180, pp. 84–86.

The elements with the smallest atomic volumes have the greatest hydrating power. When these atoms appear as ions they frequently have the smallest velocities. Therefore, the ions with smallest velocities have the greatest hydrating power. To discuss the relations somewhat in detail, the atomic volumes of potassium, rubidium, and caesium increase rapidly with increasing atomic weight, and their salts generally crystallize without water. The atomic volumes of sodium and lithium are less than half that of potassium, and yet their ionic velocities are only about two-thirds that of potassium. It will be recalled that salts of sodium and lithium may crystallize with 2 or 3 molecules of water. We may therefore assume that the increase in the volume and mass of the lithium and sodium ions, due to the formation of a hydrate, decreases the velocity of these ions below that of potassium.

The small velocity of the lithium ion was, as we have seen, for a long time unexplained. Lithium has a volume only about half that of sodium, and the largest ascertained amount of water with which the salts of lithium crystallize is 3. The maximum amount for many of the salts of sodium is 2. The lithium ion is, in general, more hydrated than the sodium ion, and its velocity is therefore decreased more by hydration. Notwithstanding its smaller volume and lighter mass, on account of its greater hydration lithium moves with about the same velocity as sodium.

The calcium atom is slightly larger than sodium, but the calcium ion has considerably smaller velocity. This is undoubtedly due primarily to its much greater hydrating power. Within this group the atomic volumes increase with increasing atomic weight. The velocities of calcium and strontium, with many salts crystallizing with 6 molecules of water, are approximately equal to that of barium. Many of the salts of barium crystallize with 2 molecules of water or water-free. The larger mass of the barium atom itself diminishes the velocity. Magnesium, with about half the volume of calcium, has nearly the same velocity, due to its greater hydrating power. The cobalt, nickel and copper atoms have nearly the same volumes and approximately the same hydrating power. Their ions have approximately the same velocities.

The atomic volumes of chlorine, bromine, and iodine are approximately the same. If, as ions, they hydrate at all we should expect the same order of hydration for all three, as has been made probable. We should expect them to have velocities of the same order of magnitude, and such is the fact.

The silver ion is the only well-established exception. Silver has a small volume and many of its salts crystallize without water. Although it has small volume, it apparently has but little hydrating power. Notwithstanding its considerable mass, with its small volume and small hydrating power we should expect it to have a fairly high velocity. The fact is, the velocity of the silver ion is slightly less than that of chlorine, bromine, and iodine.

The general truth of the relation that the ions with the smallest velocities have the greatest hydrating power is, then, established by the facts, the great hydrating power being one of the factors conditioning the small velocity.

CHAPTER XV

THE SOLVATE THEORY OF SOLUTION

Hydrate Theory for Aqueous Solutions Becomes the Solvate Theory for Solutions in General. — The earliest work on the problem of the nature of solution was limited to water as the solvent. It was found that salts in general have the power to combine with more or less of the water in which they are dissolved — have a greater or less hydrating power. This power is, however, possessed to a very different degree by the different compounds.

It having been made probable that hydration exists in aqueous solution, the question arose, do dissolved substances have the power to combine with other solvents in which they are dissolved?

To test this Jones and Getman[1] studied, by the boiling-point method, solutions of lithium chloride and nitrate and calcium nitrate in ethyl alcohol. They used also a number of other salts. It was found that the molecular rise in the boiling-point was not only greater than the theoretical rise at nearly all of the concentrations studied, but the molecular rise increases rapidly with the concentration of the solution. The molecular rise of the boiling-point of ethyl alcohol, produced by lithium chloride, increases from 1.28° at 0.07 normal to 2.43° at 2.07 normal. In calculating the theoretical molecular rise the dissociation is, of course, taken into account. The dissociation decreases with the concentration, which would tend to decrease the molecular rise in the boiling-point. Notwithstanding this influence, we have seen that the molecular rise in the boiling-point of solutions of certain salts in ethyl alcohol increases as the concentration of the solution increases.

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[1] *Amer. Chem. Journ.*, **32**, 338 (1904).

The differences between the theoretical and the experimental results are in some cases quite large. Jones and Getman[1] interpreted these results in ethyl alcohol in a manner analogous to that which they had adopted in the case of aqueous solutions. The abnormally large rise in the boiling-point of ethyl alcohol, produced by certain salts, and the increase in the molecular rise of the boiling-point with increase in the concentration of the solution, are due to combination between the dissolved substance and part of the solvent — to the formation of alcoholates in solution. The part of the alcohol that is combined with the dissolved substance is thus removed from the field of action as far as solvent is concerned. There being less alcohol present acting as solvent, the rise in its boiling-point produced by a given amount of dissolved substance would be larger than if all the alcohol were playing the part of solvent.

Further, if the dissolved substance combines with a part of the alcohol, the more concentrated the solution the greater the total amount of alcohol held in combination. This would explain the increase in the molecular rise in the boiling-point with increase in the concentration of the solution. This suggestion of combination between a part of the solvent and the dissolved substance explains the facts in alcoholic solutions just as well as the hydrate theory explains the facts in aqueous solutions.

The work of Jones and Getman with solutions in ethyl alcohol as the solvent was extended by Jones and McMaster to methyl alcohol. They also extended the work in ethyl alcohol as the solvent and repeated a part of the work of Jones and Getman obtaining results of the same general character as had been found by the earlier workers.

They used the boiling-point method with methyl alcohol as the solvent, and the chloride, bromide and nitrate of lithium as the dissolved salts. The molecular rise in the boiling-point, even in the most dilute solutions, was greater than could be accounted for by the dissociation. This is, of course, entirely incapable of accounting for the increase in the molecular rise with increase in the concentration of the solution, which manifests itself in the case of every salt studied in this solvent, dissociation decreasing with increase in concentration, which would tend to diminish the molecular rise in the boiling-point.

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[1] *Amer. Chem. Jour.*, **32**, 339 (1904).

The magnitude of the molecular rise in the most concentrated solutions is very large indeed. It is almost twice the boiling-point constant, or normal molecular rise for this solvent; and the dissociation of such solutions is certainly not more than 25 to 30 per cent, and probably less than this value.

These results were interpreted as were those in ethyl alcohol as the solvent — there is combination between a part of the alcohol present and the dissolved substance, forming methyl alcoholates. As the concentration increases, more and more alcohol is held in combination by the dissolved substance; consequently, there is an increase in the molecular rise of the boiling-point.

It thus seems that evidence was furnished of combination between methyl alcohol and the dissolved substance, on the one hand, and ethyl alcohol and the dissolved substance on the other. As we shall see later, evidence has been obtained of combination between acetone and substances dissolved in it; and other solvents have been brought within the scope of this work.

In every case thus far investigated there seems to be good evidence in favor of the view that there is combination between the dissolved substance and a part of the solvent present. In a word, combination of solvent with dissolved substance — solvation — seems to be a more or less general phenomenon. The original hydrate theory thus becomes the *solvate theory of solution.*

SPECTROSCOPIC EVIDENCE BEARING ON THE SOLVATE THEORY OF SOLUTION

Work of Uhler. — Work on the absorption spectra of solutions has been in progress in the author's laboratory continuously for nine years. This work was undertaken in connection with its bearing on the solvate theory of solution. What connection is there between solvation and the power of solutions to absorb light?

It is well known that absorption of light means that the wave-lengths of light set something vibrating with periods the same as their own. Selective absorption of light or the absorption of certain wave-lengths of light means that the wave-lengths absorbed set something vibrating with their own periods. Absorption of light is, then, a resonance phenomenon. Absorption of light by a dissolved substance means that something in the solution must be thrown into resonance with the light — must be set vibrating with the same periods as the light-waves. Many dissolved substances absorb certain wave-lengths only. This means that those particular wave-lengths of light find something in the solution which they can set vibrating with their own periods. Transparency means lack of resonance, opacity means resonance. The color of any given solution is determined by the wave-lengths of light which are not absorbed. A red solution is one which allows the long wave-lengths to pass through. A blue solution is one which allows the short wave-lengths to pass through. That particle in solution which is thrown into resonance by the light is called the resonator. This was formerly supposed to be the molecule or the ion, but is now thought to be the electron. Whatever the nature of the resonator, the absorption of light by dissolved substance is due to it.

The line of thought which led us to take up the study of the absorption spectra of solutions in connection with the solvate theory of solution is as follows: The absorption of light being due to a resonator, this would have different resonance when anhydrous than when combined with molecules of the solvent. In general, the resonance would be different when the resonator was unsolvated than when it was solvated. The color of the solution being due to the resonator, the solution could reasonably be expected to have different color when the resonator was solvated than when it was unsolvated. The study of the color of solutions, and the changes in the color when the resonator underwent changes in solvation, might give some clue to the changes in solvation.

It is a comparatively simple matter to change solvation in solution; it is only necessary to change the concentration of the solution. The more dilute the solution the more complex the solvates formed. We shall see that this often produces a marked change in the absorption spectra. We can diminish the complexity of the solvates by raising the temperature. Frequently this also produces marked changes in the absorption. Addition of a dehydrating agent will change the hydration of any given salt. This frequently changes the absorption spectra and the color of a solution; and there are many other ways of changing solvation. These frequently produce concomitant changes in the absorption spectra.

A salt dissolved in water may form hydrates, in alcohol alcoholates, in acetone acetonates, in glycerol glycerolates, etc. We should expect these different solvates to affect the resonator or resonators differently. We shall see that this is true.

With this idea in mind, work was begun in this laboratory on the study of the absorption spectra of solutions. The first investigation was carried out by Dr. Uhler and the writer. The work consisted largely in devising a method and apparatus for studying the property of solutions to absorb light. The key to the method consisted in using a grating instead of a prism spectroscope. This gave much greater dispersion, and brought out many new lines and bands. A form of cell was devised for holding solutions in non-aqueous solvents which avoided the use of all cement. The details of this phase of the work are all given in Publication No. 60 of the Carnegie Institution of Washington. The effect on the absorption spectra of increasing the concentration of the solution was studied and it was found that, in general, the effect of increasing the concentration of the solution was to widen the absorption bands. As the solvates became simpler the absorption bands became broader.

Another method of simplifying the hydrates existing in an aqueous solution was to add a dehydrating agent in the form of a second salt. It was found that this also produced a widening of the absorption bands. This was in keeping with the effect of increasing the concentration of the solution, which also simplified the hydrates.

Jones and Uhler also studied the effect of adding water to solutions in non-aqueous solvents. Thus, water was added to solutions in methyl and ethyl alcohols, acetone, etc. The effect of adding water was to narrow the absorption bands. All of these results were regarded as in keeping with the solvate theory of solution.

"Solvent Bands": Work of Anderson. — The work of Jones and Uhler on the absorption spectra of solutions was greatly extended in a number of directions by Jones and Anderson.[1] They worked with salts of cobalt, nickel, copper, iron, chromium, neodymium, praseodymium and erbium. Only that phase of the work will be discussed here which bears most directly on the solvate theory of solution. The feature of this work, which bears most directly on the solvate theory of solution, came out as the result of studying the absorption spectra of solutions of salts of neodymium and praseodymium, especially of neodymium.

Neodymium chloride was found to have quite different absorption in water from what it had in methyl alcohol. This made it desirable to study the absorption spectrum of this salt in mixtures of methyl alcohol and water. By changing the composition of the mixtures of the two solvents, one could see how the spectra corresponding to the two solvents would change.

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[1] *Carnegie Institution of Washington,* Publication No. 110 (1909). *Amer. Chem. Journ.,* **41,** 163 (1909).

It was found that when the proper mixture of alcohol and water was used, the two spectra (the one corresponding to the alcoholic solution and the other to the aqueous solution) coexisted on the plate. When the amount of water in the mixed solvents increased, the "water spectrum" came out more strongly; when the amount of alcohol present was increased, the "alcohol spectrum" came out more strongly. When the amount of water present exceeds 15 or 20 percent, we have only the "water spectrum." As the amount of water is still further decreased by the addition of more alcohol, the spectrum consists of the "water spectrum" and the "alcohol spectrum" superposed. As the amount of water is diminished below 15 percent, the intensity of the "water spectrum" becomes less and less and the intensity of the "alcohol spectrum" greater and greater.

A question of importance in the present connection is this: Does the "water spectrum" gradually change over into the "alcohol spectrum" as the amount of alcohol present is increased, or do we have here two separate and distinct spectra, the one corresponding to the aqueous solution, and the other to the alcoholic?

To test this point, fairly dilute solutions of neodymium chloride in water, in methyl alcohol, and in mixtures of water and methyl alcohol were used. The object in using dilute solutions was to be able to study the structure of the bands in the different solvents. In the more dilute solutions the several parts of any given band would come out clearly and could be measured. The result was to show that the "alcohol spectrum" was quite different from the "water spectrum." It had different components and they were arranged in a different way within the bands.

In mixed solvents, then, the two spectra coexisted, and the one did not pass over into the other as the composition of the mixture of alcohol and water was changed. The "water" spectrum and "methyl-alcohol" spectrum had equal intensities when the mixture of the water and methyl alcohol contained from 6 to 8 percent of water.

Neodymium nitrate shows change in the spectra analogous to those manifested by the chloride, when dissolved in mixtures of water and one of the non-aqueous solvents. The change with the nitrate is not so striking as with the chloride.

Praseodymium chloride in mixtures of water and methyl alcohol shows the same general features as were manifested by the chloride of neodymium. In the case of praseodymium chloride there is this additional feature: in the alcoholic solution an entirely new band appears, having no analogue in the aqueous solutions. This new band in the ultra-violet is by far the most intense in the entire spectrum of praseodymium chloride. On adding water to the alcoholic solution this band entirely disappears. In this case the alcohol spectrum is quite different from the water spectrum.

These results show beyond question that the solvent plays an important rôle in the absorption of light by solutions. The question arises, what is this rôle? It is difficult, not to say impossible, to explain the action of the solvent on any other ground than that a part of the solvent combines with the ions and molecules of the dissolved substance, the solvated parts having different resonance from the unsolvated. This means that they would absorb different wave-lengths of light. The alcoholates would have different resonance from the hydrates, whence the different absorption spectrum in alcohol from that in water.

This is important evidence in favor of solvation in solution, and, as we shall see, many examples of "solvent" bands were brought to light in the investigation which followed.

"Solvent Bands": Work of Jones and Strong. — The work of Jones and Anderson was continued by Jones and Strong.[1] They investigated a number of problems, including the effect of the solvent on the absorption of light by the dissolved substance. Jones and Anderson, as we have just seen, had found one good example of the existence of "solvent bands" in the absorption spectra of neodymium and praseodymium salts in water and the alcohols. The question arose, was this a phenomenon peculiar to these salts, or does the solvent play a general rôle in the absorption of light by solutions?

Jones and Strong attempted to answer this question by studying a large number of salts in a large number of solvents. They worked especially with salts of neodymium and uranium, because these substances had sharp absorption lines and bands whose positions could easily be determined with reasonable accuracy. Work was done not only with uranyl salts, but with uranous. A convenient method was found for reducing uranyl salts to the uranous condition, and uranous salts were found to have very sharp absorption lines.

Absorption Spectra of Uranium Compounds. — Uranyl chloride was studied in the following solvents: water; methyl, ethyl, propyl, isopropyl, butyl, and isobutyl alcohols; glycerol, ether, methyl acetate, and formamide. A comparison of the wave-lengths of the absorption lines and bands in these different solvents brought out the fact that the wave-lengths of some of the lines and bands differed considerably in the different solvents. The results here showed that the solvent unquestionably has much to do with the absorbing power of the solution, "solvent bands" appearing very frequently. The wave-lengths of a few of the different lines and bands of uranyl chloride in the above-named solvents have been tabulated,[1] and the table is here reproduced. It shows at a glance the different wave-lengths of the several lines and bands compared.

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[1] *Carnegie Institution of Washington,* Publications Nos. 130 (1910); 160 (1911). *Amer. Chem. Journ.,* **43,** 37, 224 (1910); **45,** 1(1910); **47,** 27 (1912). *Phys. Zeit.* **10,** 499 (1909). *Phil. Mag.,* **19,** 566 (1910). *Journ. Chim. Phys.,* **8,** 131 (1910).

Wave-lengths of uranyl chloride absorption lines

In water	λλ 4025,	4170,	4315,	4460,	4560,	4740,	and 4920
In methyl alcohol	λλ 4090,	4220,	4345,	4465,	4590,	4760,	and 4930
In ethyl alcohol	λλ 4100,	4250,	....	4400,	4580,	4750,	and 4900
In propyl alcohol	λλ 4100,	4230,	....	4400,	4580,	4750,	and 4910
In isopropyl alcohol	λλ 4100,	4250,	....	4360,	4560,	4750	
In butyl alcohol	λλ 4100,	4240,	....	4390,	4560,	4750,	and 4970
In isobutyl alcohol	....	....	....	λλ4400,	4560,	4720,	and 4900
In ether	λλ 4040,	4160,	....	4300,	4444,	....	and 4630
In methyl acetate	λλ 4030,	4160,	4280,	4440,	4620,	4790,	and 4920
In glycerol	λλ 4025,	4140,	4260,	4400,	4540,	4720,	and 5050
In formamide	....	....	....	λλ 4450,	4650,	....	and 4840

The absorption spectra of uranyl nitrate in mixtures of water and methyl alcohol were studied. The absorption in water was much less than in pure methyl alcohol. The addition of water to the alcoholic solution diminished the absorption. In the mixtures of water and methyl alcohol the absorption bands became very broad. A study of these broadened bands shows that they were the " alcohol " and " water " bands coexisting, and that one set of bands was not simply the other set shifted in position. The importance of this fact has already been referred to in the work of Jones and Anderson. It shows that the "alcohol" bands are fundamentally different from the "water" bands. Further, the intensity of the solvent bands is a function of the relative amounts of the solvents that are present in the mixture. This, as has been pointed out, indicates the existence of hydrates in the aqueous solutions and of alcoholates in solutions in alcohol, these solvates having definite resonance and, therefore, definite absorption spectra.

One of the most striking examples of solvent bands is shown by the absorption spectra of uranous chloride and bromide in a mixture of water and methyl alcohol. We find two entirely distinct spectra, one belonging to each solvent. Some lines and bands appear in the one solvent which are entirely absent from the other, and practically all the lines and bands have very different positions in the two solvents. To see how differently the spectra appear, reference must be made to plate 23 of Publication No. 160 of the Carnegie Institution of Washington.

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[1] *Journ. Franklin Inst.*, **176**, 528 (1913); also *Phil. Mag.*, **23**, 730 (1912).

The spectrum of uranous chloride in water is not only different from the spectrum in methyl alcohol, but these are both different from the spectrum in acetone. If we compare the spectra of this salt in the three solvents, we might easily conclude that we were dealing with three fundamentally different spectra, and the only change is in the nature of the solvent.

Uranous salts in solvents other than the above also show very characteristic "solvent" bands. When ethyl alcohol is added to an aqueous solution of uranous chloride, a marked change is produced in the spectrum. The "ethyl alcohol" bands are quite different from the "water" bands. The alcohol bands, or the water bands, can be made the more intense by simply varying the relative proportions of the two solvents. The addition of acetone to an aqueous or methyl alcohol solution of uranous chloride produces a marked change in the spectrum. A number of acetone bands appear, these being different from the " water " bands on the one hand, and from the " alcohol" bands on the other.

Uranous chloride dissolved in methyl alcohol has an absorption spectrum very similar to that in ethyl alcohol. This would be expected, on account of the close similarity of methyl alcohol and ethyl alcohol. The methyl alcohol bands are of slightly shorter wave-lengths.

The absorption spectra of uranous chloride in glycerol and in mixtures of glycerol and water were also studied. A number of "glycerol" bands manifested themselves, the glycerol absorption being very different from that of water.

The absorption spectrum of uranous chloride in methyl alcohol and ether was also studied. The solution in methyl alcohol showed complete absorption in the ultraviolet to wave-length λ 3700, while the addition of ether extended the absorption to λ 3800. The addition of the ether caused the absorption to shift towards the red, the magnitude of this shift being from 10 to 30 Å.U.

It has already been pointed out that salts of neodymium are especially well adapted to the study of "solvent" bands, on account of the sharpness of the neodymium lines and bands, and the accuracy with which they can be measured. Neodymium salts were studied in a number of solvents, and a few of the results obtained are given below.[1]

Absorption Spectra of Neodymium Chloride in Various Solvents. — The following results for the α group of absorption bands, lying in the region λ 3400 to λ 3600 obtained with noedymium chloride show the effect of the solvent on the absorption spectra of solutions of this compound. The bands of the different solvents have different wave-lengths and different relative intensities.

Having found that the solvent played an important part in determining the absorption of light by the dissolved substances, Jones and Strong used *isomeric organic solvents,* to see whether such closely related compounds would affect differently the power of substances dissolved in them to absorb light. They prepared solutions of neodymium chloride in propyl and isopropyl alcohols, and in butyl and isobutyl alcohols, and photographed the absorption spectra of this salt in these isomeric solvents. The results show different absorption lines and bands in the isomeric solvents.

If we compare carefully the spectra of neodymium chloride in butyl and isobutyl alcohols, we find that the bands are weak and diffuse in isobutyl alcohol, and have different relative intensities from what they have in the butyl alcohol. The bands in butyl alcohol are very much finer and sharper than they are in isobutyl alcohol. Further, the bands of neodymium chloride in isobutyl alcohol have slightly greater wave-lengths than in butyl alcohol.

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[1] See *Phil. Mag.,* **23,** 737 (1912), from which the few following pages are taken; also, *Journ. Franklin Inst.,* **176,** 531 (1913).

Absorption spectra of neodymium chloride in certain solvents
α GROUP

In water	In methyl and ethyl alcohols	In propyl alcohol	In isopropyl alcohol	In butyl alcohol	In isobutyl alcohol	In glycerol
λλ	λλ	λλ	λλ	λλ	λλ	λλ
3390	3475	3545	3460	3450	3455	3520
3465	3505	3460	3510	3460	3485	3475
3505	....	3490	3535	3492	3515	3550
3540	3560	3510	....	3535	3545	....
3560	....	3525	....	3545	3570	....
....	....	3540	....	3560	....	....
....	....	3560	....	....	....	....
....	....	3580	....	....	....	....

Similar results were obtained with β, γ, δ and ε groups of bands, but for these reference must be had to Publication of the Carnegie Institution of Washington, No. 210 (1915).

Absorption Spectra of Neodymium Nitrate in Different Solvents. — To eliminate the possibility of the effect of the solvent on absorption spectra being due to anything inherent in the nature of neodymium chloride, the nitrate of neodymium was studied in the same way as the chloride.

The absorption spectra of neodymium nitrate in water, in methyl alcohol, in ethyl alcohol, in mixtures of these alcohols and water, in propyl and isopropyl alcohols, in butyl and isobutyl alcohols, in acetone and in mixtures of acetone and water, in ethyl acetate and in formamide, were carefully photographed and studied. Results are given below in the case of neodymium nitrate only for the α bands.

In water. — Practically the same as the bands of neodymium chloride, but the bands of the nitrate are broader and hazier than those of the chloride.

In methyl and ethyl alcohols. — There are only two bands in the α group, λ 3465 and λ 3545.

In propyl alcohol. — λλ 3455, 3500, and 3585.

In isopropyl alcohol. — λλ 3460, 3505, and 3535.

In butyl alcohol. — λλ 3450, 3500, and 3540.

In isobutyl alcohol. — Ultraviolet absorption was so great that on the plate taken the *a* group did not appear. The absorption in general is the same as that of the chloride in this alcohol.

In acetone. — λλ 3475, and 3555.

In ethyl acetate. — λλ 3455, 3500, and 3540.

The other groups of absorption bands of neodymium nitrate in the different solvents show differences in the wave-lengths comparable with the above; but these results suffice to show the effect of the solvent on the power of neodymium nitrate to absorb light.

The above is strong evidence that the solvent plays an important part in the absorption of light by substances dissolved in it. When we take into account the number of salts studied and the number of solvents employed, the evidence is little short of proof. The only reasonable question is, how are we to interpret these facts? Before attempting to answer this question we should take into account also the following fact: A salt dissolved in a given solvent is characterized by a definite absorption spectrum. When a salt is dissolved in mixtures of varying proportions of two solvents, *only two definite absorption spectra appear,* one being characteristic of each solvent. One spectrum *does not gradually change* into the other as the composition of the mixed solvent changes, but only the *relative intensities* of the two spectra vary. Starting with that mixture of the two solvents in which both of the spectra are equally intense, if we diminish the amount of *a* relative to *b,* the spectrum corresponding to *a* becomes feebler and feebler, and the spectrum corresponding to *b* more and more intense. This fact was first noted by Jones and Anderson, and was repeatedly confirmed by the work of Jones and Strong. They found that when neodymium chloride was dissolved in a mixture of methyl alcohol and water, it showed a definite set of "water" bands and a definite set of "methyl alcohol" bands. As the amount of water in the solution was decreased relative to the alcohol, the "water" bands decreased in intensity but remained in the same position. As the amount of alcohol in the solution was decreased relative to the water, the "alcohol" bands decreased in intensity, but their position remained unchanged.

Jones and Anderson interpreted these facts as strong evidence in favor of the view that there are definite hydrates and definite alcoholates in the solution.

The spectroscopic evidence for solvation in solution furnished by Jones and Anderson has, as has already been stated, been increased many fold by the work of Jones and Strong. A large number of solvents and a fairly large number of salts have been used, and the existence of solvent bands in general has been established.

The question of the relative stability of the different solvates with respect to various physical and chemical agents has been studied at length by Jones and Strong by means of absorption lines and bands. It would lead us beyond the scope of this book to discuss these results in detail. Suffice it to say that the hydrates in general are the most persistent of all the solvates, although this depends upon the conditions to which the solution is subjected.

Transparency of Free and of Combined Water: Work of Guy. — The work on the absorption spectra of solutions, at the time that Jones and Guy began their investigation, had been extended to between 6,000 and 7,000 solutions. In all of this work the grating spectroscope had been used, and the results recorded on a photographic plate. The photographic method recorded the positions of the various absorption lines and bands, but gave only a qualitative, or at best a roughly quantitative, indication of the relative intensities of the various lines and bands. The photographic method is, generally speaking, a qualitative method.

If we are ever to discover relations of fundamental significance between the power of dissolved substances to absorb light and the nature of solution, we must have some quantitative method of studying the intensities of the absorption lines and bands and of the various parts of the same bands. With this idea in mind a very sensitive radiomicrometer was built and used to measure the intensity of absorption.

The Radiomicrometer. — The radiomicrometer not only provides us with a method of studying absorption spectra quantitatively, but greatly extends the range of wave-lengths that can be studied. The earlier work with the very sensitive radiomicrometer had to do with the study of solutions of neodymium salts. The effect of dilution on absorption spectra was also investigated quantitatively by means of the radiomicrometer. It was found by this method, as with the grating and photographic plate, that the more concentrated the solution the broader the absorption bands. It was also found that in the more dilute solution, while the absorption bands were narrower, they were more intense. Further, in the more dilute solutions the centers of the bands were displaced towards the longer wave-lengths.

Solutions More Transparent than Pure Water. — The most interesting and important result brought out by the work of Jones and Guy was the effect of the dissolved substance on the absorption of light by water. They noted that aqueous solutions of certain hydrated salts are more transparent than pure water. This is obviously a fact which called for careful study. The absorption of aqueous solutions of strongly hydrated salts was compared with the absorption of a layer of water equal in depth to the water in the solution. Similar experiments were carried out with salts which are only slightly hydrated such as potassium chloride and ammonium chloride and nitrate. It was necessary to select colorless salts which themselves had little or no absorption in the infra-red where water absorbs. It was found, in the earlier work, that the above-named compounds had nearly the same absorption as water having the same depth as the water in the solution; but in subsequent work this conclusion must be modified for certain substances near the bottoms of the absorption bands.

In terms of the solvate theory of solution, we should expect the absorption of the solution of a slightly hydrated salt in general not to differ very greatly from that of so much pure water, since, when the solvent is not combined with the dissolved substance, it is difficult to see how either could affect appreciably the absorbing power of the other.

In the case of the strongly hydrated salts, very different results were obtained. As examples of this class of substances calcium and magnesium chlorides and aluminium sulphate were studied. Take the results for a 5.3 normal solution of calcium chloride. The solution is more transparent from 0.9 μ to 1 μ. It is again more transparent from 1.05 μ to 1.2 μ, being as much as 25 percent more transparent than pure water. For the longer wave-lengths the water is in general the more transparent until 1.42 μ is reached, when both water and solution become equally opaque. Similar results were obtained with magnesium chloride.

The solvate theory seems to aid us in explaining the facts just described. Those compounds which do not form hydrates, or which form only very simple hydrates, such as potassium chloride and the like, show results such as would be expected. Their solutions are not more transparent than so much pure water. In general, the absorption of such solutions is of the same order of magnitude as that of the water in which they are dissolved. We shall see that it came out in later work that solutions of only slightly hydrated salts are more opaque than pure water at the centers of the absorption bands. This, however, does not affect at all the conclusions drawn above. It is only the hydrated salts whose solutions are appreciably more transparent than so much pure water. How does the solvate theory explain these facts?

The combined water seems to have less power to absorb light than free water. This would account for the above facts. The presence of the salt seems to shift the absorption of the water towards the longer wave-lengths. Rise in temperature and increase in concentration shift the absorption of the salt towards the longer wave-lengths. The effect of rise in temperature and increase in concentration is to simplify the hydrates existing in the solution. Simplifying the resonator, then, shifts the absorption toward the red.

The effect of the salt on the absorption of the water is the same as rise in temperature and increase in the concentration of the solution on the absorption of the dissolved substance. It may well be that the dissolved substance diminishes the association of the solvent and this simplifies the solvent resonator. This may be true, especially with water of hydration, which is more directly under the influence of the dissolved substance than the free water.

Solutions More Transparent Than Pure Water: Work of Shaeffer and Paulus. — The result obtained by Jones and Guy was regarded as of such importance in its bearing on the solvate theory of solution, that is was thought desirable to repeat and elaborate with improved method the work which led to it. Certain details of method and manipulation were carefully studied, and the degree of accuracy of the procedure adopted was carefully ascertained. The non-hydrating or slightly hydrating salts, potassium chloride, ammonium bromide, and sodium nitrate, were studied. The strongly hydrated calcium chloride, magnesium chloride, magnesium bromide, magnesium sulphate, magnesium nitrate, zinc sulphate, and zinc nitrate were investigated at varying concentrations and depths of layers.

Solutions of the strongly hydrated salts have in general greater transparency than pure water, especially at the centers of the absorption bands. As the regions of intense absorption are approached in the longer wave-lengths, the solution is much more transparent than the pure solvent. This difference may amount to as much as 40 percent.

The non-hydrated or only slightly hydrated salts give results which, in many respects, are exactly the opposite of those obtained with hydrated salts. In the three cases studied, the solution had greater absorption than the solvent at the centers of the bands. This is precisely the opposite of what was found for the strongly hydrated salts. Regions of the spectrum, for which solutions of hydrated salts were as much as 40 percent more transparent than the solvent, show for non-hydrated salts that the solution is 40 percent less transparent.

It was pointed out that the results obtained could be best explained by the solvate theory of solution. Indeed, this evidence is of the very strongest for that theory. In the solutions studied, more than half of the water was shown to be combined with the dissolved substance. It was shown that this would certainly alter the vibrational frequency or resonance of the absorbing systems.

The transmission curves obtained seem to justify the conclusion that combined water has less power to absorb light than uncombined. No other rational explanation has been found which would account satisfactorily for these results. The difference in the behavior of hydrated and non-hydrated salts seems unquestionable.

We regard, then, the spectroscopic evidence in its bearing on the solvate theory of solution as very important. The presence of definite "solvent bands" in the different solvents and the difference between the absorption of aqueous solutions of non-hydrated and strongly hydrated salts are to be counted as among the strongest and most direct lines of evidence thus far brought to light in this laboratory bearing on the solvate theory of solution.

Summary of the Lines of Evidence Bearing on the Solvate Theory of Solution. — The following lines of evidence bearing on the solvate theory of solution have, then, been established[1]; a few having been discussed in this volume.

1. Relation between lowering of the freezing-point of water and water of crystallization of the dissolved substance.
2. Approximate composition of the hydrates formed by various substances in solution.
3. Relation between the minima in the freezing-point curves and the minima in the boiling-point curves.
4. Relation between water of crystallization and temperature of crystallization.
5. Hydrate theory in aqueous solutions becomes the solvate theory in solutions in general.
6. Temperature coefficients of conductivity and hydration.
7. Relation between hydration of the ions and their volumes.
8. Hydration of the ions and the velocities with which they move.
9. Dissociation as measured by the freezing-point method and by the conductivity method.
10. Effect of one salt with hydrating power on the hydrates formed by a second salt in the same solution.
11. Investigations in mixed solvents.
12. Spectroscopic evidence bearing on the solvate theory of solution; work of Jones and Uhler.
13. Work of Jones and Anderson on absorption spectra, in which the presence of "solvate" bands was first detected. This showed that the solvate had an effect on the absorption of light, and this could be explained only as due to a combination between the solvent and the resonator, or something containing the resonator.
14. The work of Jones and Strong on absorption spectra established the existence of a larger number of "solvent" bands. They showed that these were formed by many salts and in many solvents. They could even distinguish

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[1] See *Journ. Franklin Inst.*, **176** (1913).

between the bands of a salt in a given alcohol and in its isomer. This was regarded as very important. The temperature work of Jones and Strong was strong evidence for the solvate theory.

15. The work of Jones and Guy on the effect of high temperature on the absorption spectra of aqueous solutions, and also on the effect of dilution, led to results which were all in keeping with the solvate theory.

The most important spectroscopic work of Jones and Guy which bears on the solvate theory of solution is that in which the radiomicrometer was used. It was here shown that solutions of certain strongly hydrated nonabsorbing salts are *more transparent* than pure water having a depth equal to that of the water in the solution. In the case of non-hydrated salts the solution was the more opaque. This shows that water in combination with the dissolved substance — water of hydration — has less absorption than pure, free water. This is regarded as striking evidence that some of the water in the presence of salts which are shown by other methods to hydrate is different from pure, free, uncombined water; and the simplest explanation seems to be that this is the combined water, or the water of hydration.

16. The work of Jones and Guy was repeated and extended by Jones, Shaeffer and Paulus. They obtained results of the same general character as those found by Jones and Guy. Solutions of hydrated salts were in general more transparent than pure water, especially at the centers of the absorption bands. Solutions of non-hydrated or only slightly hydrated salts are more opaque than pure water, especially at the centers of the bands.

The above sixteen lines of evidence[1] all point to the general correctness of the view that when a salt is dissolved in a solvent there is more or less combination between the salt, or the ions resulting from it, and the solvent. The magnitude of this solvation depends upon the nature of the substance and of the solvent.

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[1] For a discussion of a number of these, reference must be had to the individual papers, or to the *Publications of the Carnegie Institution of Washington.*

The limits of this volume will not permit the discussion of the development of the theory of hydration in solution along other lines than those already considered. Reference should be made, however, to the pioneer work of Pickering,[1] Nernst,[2] and Noyes,[3] as well as to the more recent contributions of Lobry de Bruyn,[4] Bousfield,[5] Buchböck,[6] Morgan and Kanolt,[7] Denison and Steele,[8] F. Dolezalek,[9] Washburn,[10] Riesenfeld,[11] and others.

How the Present Solvate Theory of Solution Differs from the Older Hydrate Theory. — The present solvate theory of solution is not simply one of several possible suggestions which accounts for a certain class of experimental facts. It is the only suggestion that has thus far been made which seems to account satisfactorily for all of the facts established. Most of the above sixteen lines of evidence bearing on solvation in solution were obtained as the direct result of experimental work suggested by the solvate theory and carried out to test this theory. Many of the results were predicted from this theory before a single experiment was carried out. Solvation, then, being accepted, as now seems pretty generally the case, the question arises, how does the present solvate theory of solution differ from the older hydrate theory of Mendeléeff, which has long since been abandoned as untenable?

Mendeléeff's theory was that certain hydroscopic substances, such as calcium chloride, sulphuric acid, and the like, formed a few definite hydrates when in the presence of water. Thus, sulphuric acid formed the hydrates $H_2SO_4.2H_2O$, $H_2SO_4.6H_2O$, $H_2SO_4.100H_2O$.

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[1] *J. Chem. Soc.*, **57**, 64 and 331 (1890); **63**, 141, 436, 890, and 998 (1893).

[2] *Nachr. Gesells. Wissensch. Göttingen*, **56**, 86 (1900).

[3] See books by this author and *Publications of the Carnegie Institution of Washington.*

[4] *Rec. trav. chim.*, **22**, 430 (1903).

[5] *Zeit. phys. Chem.*, **53**, 257 (1905); J. *Chem. Soc.*, **105**, 600 and 1809 (1914).

[6] *Zeit. phys. Chem.*, **55**, 563 (1906).

[7] *J. Amer. Chem. Soc.*, **28**, 572 (1906).

[8] *Zeit. phys. Chem.*, **57**, 110 (1907).

[9] *Ibid.*, **64**, 727 (1908); **71**, 191 (1910); **83**, 45 (1913).

[10] *J. Amer. Chem., Soc.* **31**, (1909).

[11] *Zeit. phys. Chem.*, **66**, 672 (1909); *Z. anorg. Chem*, **85**, 401 (1914).

This view of Mendeléeff was proposed, as we have seen, as the result especially of measuring the specific gravities of aqueous solutions of such compounds at different dilutions. When the specific gravities were plotted against the concentrations, the curve was not a continuous one, but showed a number of breaks. These breaks Mendeléeff could account for by assuming that certain definite hydrates or compounds between water and the dissolved substances existed at these concentrations. But before a suggestion becomes a theory there should be a fair amount of evidence supporting it, showing not only that the suggestion accounts for the facts, but that it is the only suggestion which will account for them. This was lacking in the so-called Mendeléeff hydrate theory.

The present solvate theory of solution may claim to have a fairly good experimental support, as the above review of some of the evidence obtained in this laboratory will show. In aqueous solutions hydration is a general phenomenon. Some substances combine with very little water, but most salts combine with very large amounts of water, the amount of combined water for any given substance being a function of the concentration of the solution and of the temperature. The more dilute the solution, the larger the amount of the solvent combined with the dissolved substance, i.e., the more complex the solvate. The lower the temperature the more complex he solvate. These solvates are very unstable; indeed, so unstable that it seems better to call them systems than definite chemical compounds. Anything so easily broken down by rise in temperature could hardly be called a chemical compound. Here, again, the present solvate theory differs from the older hydrate theory.

While there is some spectroscopic evidence pointing to the existence in solution of a certain definite hydrate, or certain definite hydrates, we have obtained a large amount of evidence which seems to indicate the existence in aqueous solutions of a large number of hydrates, or indeed of a whole series of hydrates, the composition depending primarily on the concentration of the solution. While this is not essential to the present solvate theory of solution, it would differentiate it fundamentally from the older hydrate theory.

The present theory is not simply a hydrate theory of aqueous solutions. Evidence has been obtained, and is herein briefly discussed, which shows that solvents other than water combine with the dissolved substance. This has been established for the alcohols by the boiling-point method, and for the alcohols and many other solvents by spectroscopic investigations. Indeed, enough evidence has already been obtained to make it highly probable that solvation is not limited to aqueous solutions, but is a general property of solutions. Solvents in general have more or less power to combine with substances dissolved in them — in a word, *we have the solvate instead of simply a hydrate theory.*

The evidence pointing to the general correctness of the solvate theory of solution is, then, so strong that it seems that this conception is in accord with a fundamental condition in connection with the nature of solution.

The question now arises, of what scientific significance or value is the establishing of the fact that there is more or less combination between the dissolved substance and the solvent?

Significance of the Solvate Theory of Solution.[1] — The evidence for the solvate theory of solution, which has been furnished in this laboratory as the result of somewhat more than a dozen years of investigation, has recently been brought together and briefly discussed.[2] The evidence is so unambiguous and convincing, that ions and some molecules combine with more or less of the solvent, that it seems that it can now be accepted as a fact of science.

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[1] The following pages are taken directly from the Author's paper in the *Journ. of the Franklin Inst.*, **176** (1913).

[2] *Zeit. phys. Chem.*, **74**, 325 (1910).

This, however, raises a number of questions: What relation does the solvate theory of solution bear to the theory of electrolytic dissociation? Does the solvate theory help us to explain any of the apparent discrepancies in the theory of electrolytic dissociation? Does the solvate theory help us to explain the facts of chemistry in general and of physical chemistry in particular? Why is the nature of solution so important, not only for chemistry but for science in general?

The Solvate Theory and the Theory of Electrolytic Dissociation. — When Arrhenius proposed the theory of electrolytic dissociation, the question was not even raised as to the condition of the ions in the solution, except that they behave as if they existed independently of one another in solution. The theory simply said that molecules of acids, bases and salts, in the presence of a dissociating solvent like water, break down to a greater or less extent into charged parts called ions, the cations or positively charged parts being electrically equivalent to the anions or negatively charged parts. The cations are usually simple metallic atoms carrying one or more unit charges of positive electricity. The cation might, however, be more or less complex, as illustrated by ammonium and its substitution products. The anion is usually complex, consisting of a larger or smaller number of atoms. It may, however, be an atom carrying negative electricity, as in the case of the halogen acids and their salts.

The degree of dissociation is determined by the nature of the acid, base or salt. Strong acids and bases are greatly dissociated. Indeed, the degree of dissociation determines their strength. Nearly all of the salts are strongly dissociated compounds, there being, however, some exceptions, as, notably, the halogen salts of mercury, cadmium, and zinc. There are, however, considerable differences in the amounts to which salts in general are dissociated at the same dilution.

The quantitative evidence furnished by Arrhenius and others for the theory of electrolytic dissociation is so convincing that few chemists of any prominence, who have carefully examined the evidence, have ever doubted the general validity of the theory; and the theory has become substantiated by such an abundance of subsequently discovered facts that it has now become a law of nature and a fundamental law of chemical science.

Arrhenius saw and pointed out clearly the importance of ions for chemistry; Ostwald and his pupils have shown that chemistry is essentially a science of the *ion*, molecules for the most part being incapable of reacting chemically with molecules; and Nernst has proved that the ion is the active agent in all forms of primary cells.

The theory of electrolytic dissociation, as already stated, does not raise the question as to the relation between the ion and the solvent. At the time that the theory was proposed, chemists did not know, and probably had no means of finding out, whether the ion is or is not combined with the solvent in contact with it. The solution of this problem remained for subsequent work.

The solvate theory of solution has been regarded in some quarters as a rival of the electrolytic dissociation theory of solution, if not directly antagonistic to it. Such is not at all the case. The solvate theory begins where the theory of electrolytic dissociation ends. The latter gives us the ions from molecules, and the former tells us the condition of the ions in the presence of a solvent after they are formed.

The solvate theory of solution, then, simply supplements the theory of electrolytic dissociation, and both must be taken into account if we ever wish to understand the phenomena presented by solution.

Does the Solvate Theory Help to Explain Any of the Apparent Exceptions to the Theory of Electrolytic Dis-

sociation? — Given the theory of solvation in solution together with that of electrolytic dissociation, the first question that arises is, does the former really aid us in explaining the phenomena presented by solutions?

Shortly after the theory of electrolytic dissociation was proposed, it was recognized and repeatedly pointed out that after all it is only a theory of "ideal solutions," *i.e.*, very dilute solutions. It was shown not to be able to explain many of the phenomena presented by even fairly concentrated solutions. Indeed, it frequently could not deal quantitatively with the very solutions with which we work in the laboratory. The explanation of this shortcoming was not fully seen, and an analogy was resorted to. It was pointed out that the laws of Boyle and Gay-Lussac for gases hold only for "ideal gases," *i.e.*, dilute gases, but do not hold for gases of any considerable concentration.

It was stated that the gas laws when applied to solutions could not be expected to hold more generally than when applied to gases, and there the matter was allowed to rest.

In the early days of the theory of electrolytic dissociation it was, however, pointed out that we have a fairly satisfactory explanation of why the simple gas laws do not hold for concentrated gases, this being expressed in the equation of Van der Waals; while no analogous explanation was offered in the case of solutions. That this point was well taken is obvious. A theory of solution, to be of the greatest value, must be applicable to all solutions, regardless of the nature of the substance, regardless of the nature of the solvent, and regardless of the concentration of the solution.

An explanation of these apparent exceptions to the theory of electrolytic dissociation presented by concentrated solutions has been furnished by the solvate theory. We now know that, for solutions in general, a part of the solvent is combined with the dissolved substance. While the amount of the solvent combined with any one ion is greater the more dilute the solution, at least up to a certain point, the total amount of the solvent in combination with the dissolved substance is greater the more concentrated the solution.

That the amount of combined solvent may become very great, even relative to the total amount of solvent present, can be seen from the following facts: In a normal solution of calcium chloride about two-fifths of the total water present is combined with the dissolved substance. In a three-normal solution of calcium chloride about five-sevenths of the total water is combined.

In the case of a normal solution of aluminium chloride in water, about five-eighths of the water present is combined with the dissolved substance, while in a two-normal solution about five-sixths of the water present is in a state of combination.

What we suppose to be a normal solution of calcium chloride is, therefore, more than one and one-half times normal, while what we suppose to be a three-normal solution is in reality more than eight times normal. In the case of aluminium chloride, what we suppose to be a normal solution is more than twice normal, while what we prepare as a two-normal solution is about twelve times normal.

These few facts, taken from thousands of a similar character, show that even fairly concentrated solutions are much more concentrated than we would suppose from the method of their preparation; while very concentrated solutions are many times more concentrated than, without the facts of solvation, we should be led to expect.

The general conclusion is that even fairly concentrated solutions are much stronger than if no solvation occurred, and are much more concentrated than we are accustomed to consider them to be from the amount of substance added to a given volume of the solvent — more or less of the water present being in combination and only the remainder playing the rôle of solvent. Without the theory of solvation, we have hitherto regarded all of the water present as acting as solvent.

We should, therefore, not expect the laws of gases to apply to such solutions, when we had no idea what was their concentration. Now that we know their concentration, we may find that the laws of gases are of as general applicability to solutions as to gases, holding not simply for dilute, but also for concentrated solutions.

The theory of electrolytic dissociation, supplemented by the theory of solvation, is, then, not simply a theory of dilute or "ideal" solutions, but a theory of solutions in general.

Does the Solvate Theory Aid in Explaining the Facts of Chemistry in General and of Physical Chemistry in Particular? — To answer this question at all fully would lead us far beyond the scope of this volume. A few facts bearing upon this question can, however, be taken up. Take, for example, the action of the hydrogen ion both in the formation and saponification of esters. In the presence of the alcohols the hydrogen ion accelerates greatly the velocity with which an ester is formed, while in the presence of water it causes the ester to break down into the corresponding acid and alcohol.

In terms of ordinary chemical conceptions it is difficult, not to say impossible, to interpret these reactions, the hydrogen ion under one set of conditions undoing what under other conditions it effects.

In terms of the solvation theory these reactions admit of a very simple interpretation. While the hydrogen ion is not strongly solvated, work in this laboratory has shown that all ions are more or less solvated. In the presence of alcohol the hydrogen ion therefore combines with a certain amount of this solvent. The hydrogen ion, plus the alcohol combined with it, unites with the organic acid, forming complex alcoholated ions which then break down yielding the ester.

On the other hand, the hydrogen ion in the presence of water combines with a certain amount of this solvent. The hydrated hydrogen ion, together with the water united with it, combines with the ester, forming a complex hydrated ion, which then breaks down into the corresponding acid and alcohol setting the hydrogen free again. For a fuller discussion of this reaction see paper by E. Emmet Reid.[1]

A reaction analogous to the above is that of hydrogen ions on amides in the presence of water on the one hand, and alcohol on the other hand. In the presence of water the hydrated hydrogen ion combines with the amide, forming a complex hydrated ion which then breaks down, yielding ammonia and acid, the ammonia, of course, combining with the acid.

In the presence of alcohol the alcoholated hydrogen ion combines with the amide, forming a complex alcoholated ion, which then breaks down into ammonia and the ester of the acid in question.

Hydrogen ions in a mixture of water and alcohol, which would contain both hydrated and alcoholated hydrogen ions, give both reactions simultaneously; but, as Reid has pointed out, in the presence of an equal number of molecules of water and alcohol, the tendency of the hydrogen ion to hydrate is greater than the tendency to form alcoholates; and under these conditions the first reaction proceeds much more rapidly than the second.[2] A very large number of types of reactions could be discussed illustrating this same point, *i.e.*, the value of the solvate theory in interpreting chemical reactions.

When we turn to physical chemical processes, the solvation of the ions has to be taken into account at every turn. The velocities of the ions are, of course, a function of the degree of their solvation; and the behavior of the ions, both chemically and physically, is a function of their velocities. The effect of dilution, and especially of temperature in reaction velocities, is largely a question of the velocities of the ions present, which, in turn, are a function of the degree of their solvation.

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[1] *Amer. Chem. Journ.* **41,** 504 (1909).

[2] *Ibid.*, **41,** 509 (1909).

In determining the actual concentration of a solution, the amount of the solvent combined with the ions must be taken into account, as has already been pointed out; and without knowing the actual concentrations of solutions quantitative chemistry would be impossible.

The solvate theory has thrown a flood of light on the whole subject of the conductivity of solutions, or the power of the ions to carry the electric current. It has shown us why the conductivity of lithium salts is less than that of sodium and potassium, notwithstanding the fact that the lithium atom is much smaller and lighter than the atom of sodium or potassium. We now know that the lithium ion is much more hydrated than the ions of the other elements, and the mass of the moving ion is really much greater in the case of lithium.

When we come to the temperature coefficients of conductivity, the solvate theory has enabled us to interpret results which, without its aid, would be meaningless. We now know why ions with the greater hydrating power have the larger temperature coefficients of conductivity. We know why ions with the same hydrating power have approximately the same temperature coefficients of conductivity, and why dilute solutions have larger temperature coefficients of conductivity than concentrated solutions;[1] and, did space permit, we could multiply examples, almost without limit, of the effect of the solvate theory on physical or general chemistry.

Why the Nature of Solution is of Such Vital Importance not only for Chemistry but for Science in General. — The fact is well recognized that modern physical or general chemistry has reached out into nearly every branch of science, and has had an important influence on many of them. The question arises: Why is this the case? The answer is that physical or general chemistry is primarily a science of solutions. And the importance of solution for science in general has already been pointed out in the introduction to this volume. An examination of the facts there referred to will show that the relation of physical or general chemistry to solutions is the prime reason why physical or general chemistry is so closely related to so many other branches of natural science. This alone would show the importance of a true and comprehensive theory of solutions, not alone for physical or general chemistry, but for the natural sciences in general.

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[1] *Amer. Chem. Journ.*, **35**, 445 (1906).

An examination of the literature on the nature of solution (Chapter II) has brought out a fact of general significance in the history of the development of any branch of science, and of any subdivision of any branch. The evolution of the subject is slow and takes place by a series of small increments, one suggestion contributing a little here and another a little there. Sometimes the steps are relatively large, but on the whole it is given to any one man of science to discover only a small amount of new truth.

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AUTHOR INDEX

Alexandrow, 281
Ambronn, 248
Anderson, 332, 335, 336, 340, 341, 346
Archibald, 208
Arrhenius, 46, 49, 80–84, 86, 87, 89, 132, 135, 197, 286, 287, 315, 351, 352
Aston, 204, 211
Avogadro, 73, 77–79

Baker, 9–11
Barnes, 207
Bartholi, 81
Barus, 275
Bassett, 215, 314
Baudouin, 257
Bechhold, 274
Beckmann, 115, 117, 118, 127, 129, 130
Berkeley, 55, 67
Bernthsen, 150
Berthelot, 40–42, 144
Berthollet, 23, 24
Berzelius, 27–30, 236
Beudant, 94, 95
Biltz, 271, 286
Bingham, 215, 216
Bizio, 72
Blagden, 122
Blake, 258, 259, 261
Boerhaave, 21
Bousfield, 348
Boyle, 5, 62, 64, 66, 73, 76, 79, 82, 89, 97, 353
Braun, 258
Bredig, 192, 193, 231, 236, 237, 260, 284, 285
Brown, R., 241
Bruni, 239
Buchböck, 348
Burton, 257, 265
Bütschli, 274

Cady, 207
Cailletet, 3, 278
Carrara, 203
Carroll, 214, 215
Centnerszwer, 206, 207
Chambers, 306
Chaperon, 95
Clausius, 33–35, 49, 81, 83, 164, 165, 246
Clover, 316
Colson, 301, 302
Coppet, 122
Cotton, 247, 255
Coulomb, 209

Dalton, 25
Davis, 208, 223–225
Davy, 27, 236
Denison, 348
DeVries, 67–71, 74
Dewar, 297
Dimitrievics, 279
Dolezalek, 348
Drude, 210
Duclaux, 258
Dutoit, 204, 211

Ehrenhoft, 243
Einstein, 243, 246
Erlich, 286
Exner, 242, 243

Faraday, 103, 104, 135, 156–158, 160, 162, 163, 188, 190, 209, 235
Favre, 38, 39, 81
Fick, 92, 93, 97
Fischer, 288

Fitzpatrick, 203
Fizeau, 248
Fourcroy, 23
Fourier, 93
Franklin, 207
Frazer, 59, 64, 66, 111, 114, 306
Freundlich, 265, 266, 274, 276, 280, 289, 293
Friderich, 204
Friedmann, 271

Galvani, 27, 196
Gay-Lussac, 25, 30, 31, 43, 48, 61, 62, 64, 66, 72–76, 79, 89, 94–97, 103, 353
Getman, 307, 310, 311, 313, 327, 328
Gibbs, 197
Gladstone, 39, 281
Gordon, 287
Gore, 302
Gouy, 95
Graham, 91, 92, 226–232, 234, 240, 284
Grotthuss, 25–27, 164
Guldberg, 35, 36, 48, 72, 135
Gutbier, 236
Guthrie, 134
Gutmann, 10
Guy, 222–224, 341, 342, 344, 347
Guye, 211

Hamburger, 70, 74
Hantzsch, 150
Hartley, 55, 67
Hauer, 303
Helmholtz, 9, 197, 254
Henderson, 153
Henry, 2, 163
Herzog, 241
Heydweiller, 174
Hibbert, 281
Hippocrates, 4
Höber, 287
Hofmeister, 278, 280
Holland, 59
Horstmann, 48, 72
Hosford, 316
Howard, 316
Howe, 225
Hughes, 8, 224
Humphrey, 120
Hyde, 207

Ikeda, 284

Jacobson, 316
Jones, 116, 118, 130, 184, 205, 207, 216, 222–225, 306, 311, 313, 314, 322, 324, 327, 328, 332, 335, 336, 338, 340–342, 344, 346, 347

Kablukoff, 203, 204
Kanolt, 348
Kattein, 238, 279
Klaproth, 23
Knight, 306
Kohlrausch, 40, 81, 172–174, 177, 178, 181, 195, 219
Kopp, 35, 93
Krafft, 290, 292
Krapiwin, 203, 213
Kraus, 207
Krause, 181
Kreider, 219, 316
Küster, 292, 304

Lagergren, 298
Landolt, 39
Lavoisier, 22–24
Lea, 230, 231, 236
Le Blanc, 166, 168, 170
Le Chatelier, 298
Lémery, 5
Lewis, 208
Lieben, 95
Liebig, 93, 105
Lillie, 238
Linder, 239, 255, 260–262, 282
Lindsay, 213
Lloyd, 209
Lobry de Bruyn, 348
Lodge, 194–196
Loeb, 191
Loew, 230
Longinescu, 211
Losev, 293

Lottermoser, 273
Lovelace, 111, 114
Lüdeking, 277, 279
Ludwig, 96

Mackay, 184
Madsen, 286
Mahin, 220
Marsden, 302
Marsh, 9
Maxwell, 246
McIntosh, 208
McMaster, 216, 328
Mendeléeff, 44–48, 72, 348, 349
Michaelis, 272
Mohler, 120
Morgan, 348
Morse, 58–60, 62–64, 66, 97
Morveau, 22
Moser, 95
Mouton, 247, 255
Murray, 214
Muthmann, 230
Myrick, 66

Nägeli, 284
Neisser, 271
Nernst, 161–163, 191, 197–199, 209, 348, 352
Newton, 20
Noyes, A. A., 154, 155, 181, 348

Offer, 134
Ohm, 93
Onnes, 175
Ostwald, Wilhelm, 105, 129, 130, 145–150, 159, 161–163, 175, 178–180, 186, 187, 201, 315, 317, 352
Ostwald, Wolfgang, 233, 280
Ota, 306

Paal, 289
Palmaer, 198
Pappada, 239
Paracelsus, 5
Pauchon, 104
Pauli, 259, 284
Paulus, 344, 347
Pearce, 130, 315, 322, 324
Perrin, 243–246, 254, 257
Pfeffer, 50–55, 58, 71–74, 77, 97, 238
Pfund, 297
Pickering, 348
Pictet, 3
Picton, 239, 255, 260–262, 282
Pincussohn, 272
Proust, 24
Putnam, 208, 224

Quinke, 254, 257

Ramsay, 119, 120, 211, 212, 214, 243
Raoult, 43, 44, 49, 81, 106–111, 122–127, 132, 133, 238, 240, 281, 311
Rayleigh, 111
Raymond, 163, 294
Reid, 356
Reinders, 285
Reinke, 278, 279
Reuss, 254
Richartz, 9
Riesenfeld, 348
Roberts-Austin, 302
Robinson, 194
Rodewald, 238, 279
Rose, 13, 14
Rosenstiehl, 72
Rouiller, 216
Rowland, 120
Rudolphi, 180

Sabanejew, 281
Sachkanov, 177
St. v. Gorski, 204
St. v. Laszczynski, 204
Schlamp, 203
Schmidt, 221, 222, 293
Selmi, 226
Shaeffer, 316, 344, 347
Shields, 211, 212, 214
Siedentopf, 247–250
Smith, 316
Smits, 290
Smoluchowski, 243
Sörensen, 153
Soret, 75, 76, 96, 97

Spring, 300, 301
Springer, 316
Stas, 10, 11
Steele, 348
Stern, 290
Stieglitz, 150, 151
Stokes, 245–247
Strong, 335, 338, 340, 341, 346, 347
Svedberg, 237, 242, 243

Tammann, 104
Thales, 4
Thomsen, 41–43, 48, 72
Thomson, 25, 26, 28, 121, 148, 206, 209
Traube, 50
Tyndall, 247

Uhler, 330–332, 346

Valentine, 4
Valson, 36, 38, 39, 44, 49, 81
Van Bemmelen, 276, 298
Van der Waals, 89, 353
Van Helmont, 4, 5
Van't Hoff, 31, 48, 63, 72–74, 76–80, 82, 84, 86, 89, 118, 128, 129, 132, 135, 181, 196, 197, 298–304
Vaubel, 298
Veazey, 217, 222, 224, 225
Violle, 302
Völlmer, 203
Volta, 27, 196
Von Berneck, 284, 285
Von Meyer, 373
Von Schröder, 277, 278
Von Weimarn, 283

Waage, 35, 36, 48, 72, 135
Walden, 205, 206
Walker, 105
Wallerius, 22
Wanklyn, 8
Washburn, 348
Wenzel, 280
Werner, 204
West, 316
Whitney, 258, 259, 261
Wiedemann, 254, 279
Wiener, 242
Wiesel, 209
Wight, 316
Wightman, 209, 316
Williamson, 31–33, 48, 81
Winston, 316
Witt, 292
Wladimiroff, 70
Wöhler, 93
Wroblewski, 3
Wüllner, 95, 104

Zanniovich-Tessarin, 205
Zelinsky, 203, 213
Zsigmondy, 236, 247, 248, 250–252, 273

SUBJECT INDEX

ABNORMAL electrolytes, 206
Absorption of light by solutions, 330
— spectra of solutions, effect of dehydrating agents on, 332
— — — effect of solvent, 332, 334
— — — of neodymium salts, 333, 338
— — — of uranium salts, 335
— — — relative transparency to solvent, 342
— — — solvent bands, 332, 335, 339
— — — use of radiomicrometer, 342
Acetone, conductivities in mixtures containing, 215, 224
Acid, definition of, 136
Acids, dissociation of, 183
Active and inactive molecules, 83
Activity coefficients (Arrhenius), 83
Adsorption, application to high vacua, 297
— effect of solvent on, 295
— — temperature on, 296
— history of, 294
— in soils, 288
— theories of, 297
— theory of colloids, 282
Aggregation, states of, 2
Alcohol, conductivities in mixtures containing, 213, 215, 221
"Alkahest," 5
Ammonia, dissociating power of liquid, 207
Amphoteric compounds, and biology, 152
— — dissociation of, 151
Amplitude of Brownian movement, 242
Analogy between solutions and gases, 30, 42, 72
Antitoxins and toxins, 286
Association, and dissociating power of liquids, 211
Association, effect of temperature on, 212
— factors of liquids, 212
Atomic volume, and viscosity, 218
— mass from Brownian movement, 246

BASE, definition of, 137
Bases, dissociation of, 183
Berthollet's chemical theory of solution, 23
Berzelius' electrochemical theory, 27
Boiling-point apparatus, (Jones), 116
— method (Beckmann), 115
— — electrolytic dissociation by, 118
— — molecular weights by, 117
Brownian movement, 241
— — amplitude of vibrations in, 242
— — and kinetic theory, 246
— — and precipitation of colloids, 262
— — and ultramicroscopy, 251
— — and viscosity of media (Svedberg), 242
— — mass of atom from, 246
— — Perrin's work on, 243
— — theories of, 243
— — velocity of particles in, 242

CAPILLARY moduli, law of (Valson), 36
Carbon dioxide, geological action of, 13
Catalysts, action of "poisons" on, 285
Cataphoresis, 254
Cells, primary, 196
Chemical action, gravitational theory of (Newton), 20
Chemical equilibrium, importance of recognized (Williamson), 31

Chemical inactivity in absence of water, 6
— — — — of hydrochloric acid and carbonates, 8
— — — — of acids on litmus, 9
— — — — of hydrochloric acid and ammonia, 9
— — — — of sulphuric acid and sodium, 11
Colloidal particles, size of and ultramicroscope, 250
Colloidal preparations, chemical methods, 234
— — electrical methods, 234, 236, 284
— — hydrolysis methods, 234
— — reduction methods, 235
Colloidal solutions, as catalysts, 285
— — fundamental properties of, 237
— — of metals, 231, 236, 284
— — precipitation of, 260
— — — action of electrolytes, 261, 264
— — — and valency of precipitating ion, 265, 268
— — — microscopic phenomena, 262
— — preparation of, 234
Colloids, adsorption theory of, 282
— and agriculture, 288
— and mineralogy, 289
— and pharmacology, 287
— early history of, 226
— electrical properties in nonaqueous solutions, 257
— Graham's work on, 227
— industrial applications of, 289
— mutual precipitation of, 271
— relation to physiological chemistry, 284
— suspension theory of, 282
— theory of precipitation of, 263, 283
Color in solution, cause of, 145
— — — and electron theory, 147
— — — and theory of electrolytic dissociation, 146
Conductivities, in acetone mixtures, 215
— in alcohol mixtures, 213
Conductivities, in glycerol, 221
— in mixed solvents, 213
Conductivity, electrical, at high temperatures, 181
— — theory of, 171
— — method, Kohlrausch, 40, 172
— — of solutions, law of, 177
— of suspensions, 258
— water, 174
Cryohydrates, 133

Decomposition values of electrolytes, 167
Dialysis, 231
— Graham's method, 228
Dielectric constants, determination of (Drude), 210
— — effect of on dissociating power of liquids, 209
— — of liquids, 211
Diffusion, 90
— and osmotic pressure, 96
— effect of mass on, 95
— generalization of Fick, 93
— Graham's work on, 91, 227
— in solids, 301
— of sols, 240
— temperature coefficients of, 96
Dilution law, Ostwald, 179
— — Rudolphi, 180
Dissociating power, and association, 211
— — and dielectric constants, 209
— — of liquid ammonia, 207
— — of liquids, relative, 203
— — — Walden's work on, 205
Dissociation, electrolytic, and dilution, 179
— — by boiling-point method, 118
— — comparison of freezing-point and conductivity measurements of, 315
— — by freezing-point method, 129
— — in acetone, 204
— — in alcohols, 203, 209
— — in ether, 204
— — in formamide, 208, 224
— — in formic acid, 205

Dissociation, electrolytic, in hydrocyanic acid, 206
— — in hydrogen dioxide, 207
— — in inorganic liquids, 205
— — in nonaqueous solvents, 219
— — in pyradine, 204
— — in ternary mixtures, 220
— — in water, 183
— — — of acids, 183
— — — of bases, 183
— — — of complexes, 184
— — — of salts, 184
— — theory of, 82
— hydrolytic, 153
Dyeing, 291
— and adsorption, 293
— and chemical action, 292
— and solid solutions, 293
Dynamics, chemical, importance recognized, 143

Electrical charge and precipitation of colloids, 271
— dispersion, 236
— properties of sols, 252
Electrochemical theory of Berzelius, 27
Electroendosmose of sols, 253
— effect of electrolytes on, 254
Electrolysis and conductance, 161
— primary of water, 170
— theories of, 27, 33, 164, 166
— theory of and decomposition values, 167
Electrolytes, abnormal, 206
— action of on colloids, 261
— decomposition values of, 167
— osmotic pressure of, 64
Electrolytic dissociation, by boiling-point method, 118
— — by conductivity method, 178
— — by freezing-point method, 129
— — early conceptions of (Grotthuss), 25
— — methods of measuring, 83
— — theory of, 82, 87, 351
Electrostenolysis, 258
Emulsions, 233
Emulsions, electrical properties of, 259
— precipitation of, 273
Emulsoids, 233
— osmotic pressure of, 238
— precipitation of, 270, 273
Enzymes, 285
Ether formation, theory of (Williamson), 31

Faraday's laws, 156
Ferments, organic and inorganic, 284
— catalytic action of, 285
Formamide, dissociation in, 208, 224
Formic acid, dissociation in, 205
Freezing-point investigations, 122, 130
— lowering, abnormal, 306
— — and water of crystallization, 308
— — bearing on hydration, 309
— — by sols, 239
— — in solid solutions, 304
— — Raoult's law of, 43, 126
— method (Beckmann), 127
— — molecular weights by 128
Fusible metals, 304

Gases, analogy between solutions and, 30, 42, 72
— liquefaction of, 3
Gelatine, 270
Gelation, 234, 270
Gels, 232, 274
— honeycomb structure of, 275
— imbibition by, 277
— less elastic, 276
— more elastic, 277
— physical properties of, 275
— solventation of, 276
Glycerol, conductivities in, 221
— viscosities in, 222
Gold number, 273

Heat of neutralization, 139
Hydrates, composition of, 310
— early views on, 41
— of sulphuric acid, 45, 47, 349
— theories of, 44, 307, 348

Hydration, and atomic volume, 322
— and ionic velocity, 193, 324
— and osmotic pressure, 62
— and temperature coefficients of conductivity, 316
— of gels, 276
— relative of anion and cation, 324
Hydrolysis, 153
Hydrolytic dissociation, 153
— — effect of temperature on, 153
Hydrosols and hydrogels, 232

Imbibition, 277
— calorimetry of, 279
— effect of solutions on, 280
— pressure from, 278
— rate of by gels, 278
— volume changes in, 277
Indicators, ionization constants of, 151
— Ostwald theory of, 149
— Stieglitz's work on, 150
Ionic theory, 87
Ions, 83
— absolute velocity of, 194
— apparatus for measuring velocity of, 188
— effect of concentration and temperature on velocity of, 190
— hydration of and atomic volume, 322
— modes of formation, 186
— relative velocities of, 188, 192
— velocity of and hydration, 193, 324
Ionization constants, 84
— of indicators, 151
Isohydric solutions, 185
Isosmotic solutions, 69
Isotonic coefficients (De Vries), 69

Kinetic theory, and Brownian movement, 246
Kohlrausch conductivity method, 172
— law, 40, 177

Lavoisier's conceptions of solution, 22
Liquefaction of gases, 3
Liquids, association factors of, 212
— dielectric constants of, 211
— relative dissociating power of, 203
— solvent power of, 202
— Walden's work on dissociating power of, 205
Lyophile — lyophobe sols, 234

Mass-action, law of (Guldberg and Waage), 14, 36
Mercury, molecular weights of metals in, 119
Metals, colloidal solutions of, 231, 236, 284
— molecular weights in mercury, 119
— solution tension of, 197, 200
Migration velocities of ions, 40, 177, 188, 192, 195
Mixed solvents, conductivities in, 213
Moduli of coersion (Farve and Valson), 38
Molecular weights, by boiling-point method, 117
— — by freezing-point method, 128
— — of metals in mercury, 119
Mordaunts, 292

Negative sols, 255
— — precipitation of, 266
— viscosity coefficients, 218, 223
Neutralization, 137
— heat of, 139
Nomenclature of colloidal chemistry, 231, 233
— of ultramicroscopy, 249
Nonaqueous solvents, dissociation in, 202, 204, 219

Osmotic pressure, and diffusion, 96
— — and Boyle's law, 73
— — and Gay Lussac's law, 74
— — application of gas laws to, 72
— — cell for high (Frazer), 66
— — durability of cells, 66
— — in solid solutions, 300
— — measurements of Pfeffer, 50
— — membranes by electrical endosmose (Morse), 58

Osmotic pressure, Morse's method of measuring, 59
— — of cane sugar, 60
— — of concentrated solutions, (Berkley and Hart), 55
— — of electrolytes, 64
— — of emulsoids and suspensoids, 238, 239
— — of glucose, 63
— — relation to gas pressure, 60, 77
— — relative, 67, 70
— — rôle in different sciences, 99
— — Traube's method of measuring, 50
Ostwald dilution law, 179
— theory of indicators, 149

Poisons, catalytic, 285
Positive sols, 255
— — precipitation of, 265
Precipitation of colloids, and Brownian movement, 262
— — protective effect, 273
— — valency rule, 268
Primary cells, 196
— — Nernst's work on 198
Protective effect and colloidal precipitation, 269, 273
Purple of Cassius, 236

Radiomicrometer, 342
Raoult's laws, 111, 127
Resonance, 145, 330

Salts, dissociation of, 184
— thermoneutrality of, 142
Selective absorption of light by solutions, 330
Semicolloids, 289
Semipermeable membranes (Morse), 58
— — preparation of (Traube), 50
Silver, colloidal, (Lea), 230
— ion and theory of hydration, 326
Soaps, 290
Size of colloidal particles and ultramicroscopy, 250
Solation, 234
Solids, diffusion in, 302
— osmotic pressure in mixtures of, 301
— vapor-tension, lowering of, 303
Solid solutions, kinds of, 299
Sols, boiling-point, freezing-point, and vapor pressure of, 239
— diffusion of, 240
— electrical properties, 252
— mutual precipitation, 271
— precipitation of, 260
Solution, Lavoisier's conception of, 22
— law of electrical conductivity of, 177
— modern definition of, 2, 6
— rôle of in different sciences, 12–16
— theories of, chemical, Klaproth, 23
— — — Berthollet, 23
— — — Kopp, 35
— — — Thomson, 25
— — mechanical, Lavoisier, 23
— — — Fourcroy, 23
— — 17th and 18th century, Newton, 20
— — — Boerhaave, 21
— — — Wallerius, 22
Solutions, and gases, 30, 42, 72, 78
— as compounds (Kopp), 35
— fundamental properties, 132
— isohydric, 185
— law of electrical conductivity of, 177
Solution-tension of metals, 197
— — proof of, 198
— — values for, 199
Solvate theory, and chemistry in general, 355
— — relation to theory of electrolytic dissociation, 357
Solvation, and selective absorption of light, 331
— in nonaqueous solutions, 329
— in the alcohols, 327
— summary of evidence for, 345
Solvent bands, 332, 335, 337, 341
Solvents, nonaqueous, dissociation in, 202, 219
Soret, principle of, 75, 96

Surface tension, 263, 285, 297
Suspensions, 233
— action of electrolytes on, 261, 269
— conductivity of, 258
Suspension theory of colloids, 282
Suspensoids, 233
— osmotic pressure of, 239
— precipitation of, 260

Tanning, 291
Temperature coefficients of conductivity, and relative hydrating power, 321
— — — of strongly hydrated salts, 319
— — — of weakly hydrated salts, 318
— effect of on adsorption, 296
— — on association, 212
Ternary mixtures, dissociation in, 220
Theory of electrolytic dissociation, 82, 87, 351
Thermochemical investigations, Berthollet, 40
— — Thomson, 42
Thermoneutrality of salts, 142
Toxins and antitoxins, 286
Transmission of light, relative by solvent and solution, 345
Tyndall effect, 247

Ultramicroscope, 247
— applications of, 249
Ultramicroscopy, nomenclature of, 249
Universal solvent, 5

Vacua, high by adsorption, 297
Valence, nature of chemical, 158
Vapor pressure lowering, in solid solutions, 303
Vapor-tension, early work on, 103–105
— — effect of concentration on, 107
— — — solute, 109
— — — solvent, 110
— — — temperature, 108
— — lowering of by sols, 239
— — measurements, Walker, 105
— — — Frazer-Lovelace method, 111
— — of nonaqueous solutions, 106
— — Raoult's work on, 106
Velocity of ions, 188
— absolute, 194
— apparatus for measuring, (Jones), 189
— effect of concentration and temperature on, 190
— relative, 188, 192
— — and atomic volume, 193
Velocity of particles in cataphoresis, 255
Viscosity, 217
— and Brownian movement, 242
— negative coefficients of, 218, 223
— of glycerol solutions, 222
— of rubidium and caesium salts, 223
— relation to atomic volume, 218

Water, as the original element, 4
— chemical and physical properties of, 17
— chemical inactivity, in absence of, 7
— dissociation of solutions in, 183
— importance of in chemical reactions, 138
— of crystallization, and hydration, 308
— — and temperature, 314
— purification of for conductivity, 174
— theory of primary electrolysis of, 170

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